THE SOAP AND DETERGENT ASSOCIATION

A COMPUTER MODEL FOR PHOSPHATE PRECIPITATION WITH ALUM AND FERRIC CHLORIDE

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OBJECTIVES

The objectives of this study were to develop, test and utilize an empirical chemical equilibrium model to predict the chemical doses (ferric chloride or alum) required to achieve a given dissolved orthophosphate (ortho-P) residual in simultaneous precipitation processes for a range of influent dissolved ortho-P, total alkalinity and pH values.

NEED FOR STUDY

The removal of phosphate to low levels (in the range 0.2 - 2 mg total P/l) is an effluent criterion for waste treatment plants in several regions of the United States (e.g., Great Lakes Basin, Chesapeake Bay, Florida). With the typical ranges of waste characteristics for USA municipal wastewaters, the conventional secondary treatment combination of primary sedimentation and biological treatment (activated sludge or trickling filters) cannot be counted upon to achieve P residuals in this range. Two general methods are utilized to achieve these residual levels -- chemical precipitation of phosphate and enhanced biological phosphorus removal. This study addresses the use of chemical precipitation to achieve lower P residuals. Phosphate precipitating agents utilized in waste treatment commonly are salts of iron (ferric and ferrous chlorides and sulfates), aluminum (alum) and calcium (lime). The most widely used in the USA are iron and aluminum salts, possibly because they are effective at pH values consistent with their application simultaneously into biological secondary treatment process units such as activated sludge aeration basins. It is the use of such materials in the simultaneous precipitation mode that will be addressed in this study, although the model developed is equally applicable to phosphate precipitation in primary treatment or tertiary treatment processes.

One of the sources of phosphate in municipal wastewater is detergent products containing polyphosphate-based additives (builders). The contribution of detergent phosphate to the total phosphate content of municipal wastewater has been variously estimated. Booman (1984) has given the value of 0.4 kg P/capita year as the detergent P contribution to a total domestic sewage P content of 1.4 kg P/capita year.

In view of the "identifiable" and "controllable" nature of the detergent P contribution to wastewater, much activity has been devoted to ban or reduce the amounts of P in detergents. One of the rationales for such actions is that if a wastewater treatment plant must utilize chemicals to achieve its effluent P residual, reducing the influent P will reduce the chemical dose required and the mass and volume of sludge to be treated. The magnitude of these reductions has been a topic of discussion for many years. It was the major objective of this study to provide a rapid and rational method for estimating chemical doses to achieve a desired P residual based on sound principles and operationally derived chemical equilibrium data.

APPROACH TO PROBLEM

The problem was approached by a review of the literature to select a model that was rational and sufficiently comprehensive to allow its application to a wide range of conditions of waste characteristics, P residuals and chemical doses. The model selected was that of Ferguson and King (1977). Additional input was obtained from Ferguson (1972).

NATURE OF THE MODEL

The Ferguson and King (1977) model is divided into two general parts:

1. The model calculates the pH of the wastewater after the precipitant dose has been added.

2. The model calculates the P residual under one of three chemical cases, which are internally verified during the model calculations. These are:

a. No precipitate Insufficient alum has been added to precipitate aluminum phosphate; the addition of alum changes the pH.

b. One precipitate Only aluminum phosphate precipitates. In this regime the removal of P can be determined by stoichiometry (at low alum doses) or by the solubility product of aluminum phosphate (at higher alum doses).

c. Two precipitates Both aluminum phosphate and aluminum hydroxide precipitate. The P residual is determined by equilibria between the solids.

Assumptions that are made in the use of the model and in the values of the input terms include:

1. Equilibrium as described by the stated equilibrium constants is achieved. Kinetics are not considered. However, since many of the equilibrium constants (especially those describing heterogenous reactions) are based on operational data most likely with amorphous rather than crystalline solids, kinetics may well be tacitly included.

2. The systems are assumed to be closed to the atmosphere with respect to exchange of CO_2.

3. Mixing of chemicals is assumed excellent and the same from case to case.

4. The models apply only to the precipitation of dissolved ortho-P. The removals of influent particulate P are not considered. Dissolved condensed P is assumed not to be present. This is justified on the basis that the models are applied to simultaneous precipitation and that the biological treatment system has had the opportunity to hydrolyze the condensed P to ortho-P.

5. The model does not predict biological uptake of P by the organisms in secondary treatment processes. In simultaneous precipitation

processes the biological uptake of P is assumed to take place before the removal of P by chemical precipitation. Because of these assumptions it was necessary to generate a range of values of soluble ortho-P which might be typical of those influent to the precipitation process. This was done as follows:

- Assume 3 values of per capita sewage volume (100, 150 and 200 gal/cap.- day).
- Assume per capita BOD_5 (BOD) contribution = 80 g/cap.-day.
- Assume total per capita P contribution = 1.4 kg/cap.-year = 3.84 g/cap.-day.
- Assume detergent P contribution = 0.4 kg/cap.-year = 1.1 g/cap.-day.
- Assume BOD_5 removal by primary sedimentation = 35%.
- Assume total P removal by primary sedimentation = 10%.
- Assume activated sludge production = 0.65 kg TSS/kg BOD_5 removed.
- Assume activated sludge P content = 2% of TSS.

Then (for example) for a 100 gal/cap.-day sewage flows, and with no detergent P ban:

Raw sewage BOD_5 concentration (mg/l) =

$$\frac{80 \text{ g BOD}}{\text{cap.-day}} \times \frac{1000 \text{ mg}}{\text{g}} \times \frac{\text{gal}}{3.785 \text{ l}} \times \frac{\text{cap.-day}}{100 \text{ gal}} = 211 \text{ mg/l}$$

Primary effluent BOD_5 (mg/l) = 211 - (211 x 0.35) = 137 mg/l

Raw sewage total P concentration (mg/l):

$$\frac{3.84 \text{ g P}}{\text{cap.-day}} \times \frac{\text{gal}}{3.785 \text{ l}} \times \frac{\text{cap.-day}}{100 \text{ gal}} = 10.1 \text{ mgP/l}$$

Primary effluent total P (mg/l) = 10.1 - (10.1 x 0.10) = 9.1 mg P/l

P removal by activated sludge =

$$\frac{137 \text{ mg BOD}}{1} \times \frac{0.65 \text{ mg TSS}}{\text{mg BOD}} \times \frac{0.02 \text{ mg P}}{\text{mg TSS}} = 1.8 \text{ mg P/l}$$

Therefore P available for chemical removal = 9.1 - 1.8 = 7.3 mg P/l.

Results of the calculations for each of the cases considered are presented in Table 1. From these calculations it was decided to use the "No detergent P ban"/"Detergent P ban" influent soluble ortho-P pairs of values of 7 and 5 mg P/l, 5 and 3 mg P/l, and 4.0 and 2.5 mg P/l.

6. The P residuals considered (and predicted) by the model are soluble ortho-P residuals. It should be recognized that effluent standards usually are stated in terms of total P concentration and include particulate P. This is not predicted by the model but must be estimated separately from a knowledge of the effluent suspended solids concentration and the P content of the suspended solids. Typical values of effluent total P standards are 0.2, 0.3, 0.5, 1.0 and 2 mg P/l. Table 2 gives the soluble ortho-P concentration that would have to be achieved at various effluent suspended solids concentrations in order to meet these effluent total P standards. The suspended solids are assumed to contain 2% P. On the basis of Table 2 it would seem pertinent to consider chemical doses required to produce soluble ortho-P residuals of 0.1, 0.3, 0.5, and 1.5 mg P/l to cover the range of interest. For the sake of completeness and to provide for an evenly distributed data output, soluble ortho-P residuals of 0.8 and 1.1 mg P/l also were considered.

TABLE 1 Development of Initial Soluble Orthophosphate for "No Detergent Ban" and "Detergent P Ban" Situations

Sewage Volume gal/cap-day	Raw BOD_5 mg/l	Primary BOD_5 mg/l	No Detergent Ban			Detergent Ban		
			Raw P mg/l	Primary P mg/l	P after biol. treat+ mg/l	Raw P mg/l	Primary P mg/l	P after biol. treat+ mg/l
100	211	137	10.1	9.1	7.3	7.2	6.5	4.7
150	140	91	6.8	6.1	4.9	4.9	4.4	3.1
200	106	69	5.1	4.6	3.7	3.6	3.3	2.4

TABLE 2. Soluble Ortho-P Concentrations Required to Meet Various Effluent Total P Requirements at Various Effluent Suspended Solids Concentrations (Effluent SS = 2% P)

Total Phosphate (mg P/l)	Effluent Suspended Solids (mg/l)	Phosphate in Suspended Solids (mg/l)	Required Soluble Orthophosphate (mg P/l)
0.2	5	0.1	0.1
0.3	5	0.1	0.2
0.3	10	0.2	0.1
0.5	5	0.1	0.4
0.5	10	0.2	0.3
0.5	20	0.4	0.1
1.0	20	0.4	0.6
1.0	30	0.6	0.4
2.0	20	0.4	1.6
2.0	30	0.6	1.4

7. Input values for initial wastewater total alkalinity were 100, 200 and 300 mg as $CaCO_3$/l -- a range that covers most wastewaters. Similarly, the chosen initial wastewater pH values of 7.0 and 7.5 are typical of the range of values found in practice for primary domestic wastewater effluents.

8. Wastewater total alkalinity is an input variable in the model. One of the potential poly-P replacements in detergents is sodium carbonate (washing soda). The effect on the wastewater total alkalinity of replacing detergent poly-P with sodium carbonate was found to be negligible using the following rationale (and using "rounded" numbers for illustration):

a. Assume total wastewater alkalinity = 100 mg $CaCO_3$/l. This is a low alkalinity for a wastewater so that the effects on alkalinity are maximized. The total alkalinity includes contributions from the carbonate system and from phosphates.

b. Assume influent P concentration = 7 mg P/l (1.36 kg /cap.-yr. at waste flow of 150 gal/cap.-day).

c. Assume detergent P = 2 mg P/l (0.4 kg P/cap.-yr. at waste flow of 150 gal/cap.-day)

d. Assume 100% Na_2CO_3 replacement of detergent P, resulting in a detergent that contains 20% Na_2CO_3 and contributes 1.3 kg Na_2CO_3/cap.-yr.

Total alkalinity = 100 mg $CaCO_3/l$ = 2 meq/l

Detergent phosphate alkalinity = 2 mg P/l x $\frac{2\ \text{meq}}{\text{mM}} \times \frac{1\ \text{mM}}{31\ \text{mg P}}$

= 0.13 meq/l

Therefore, carbonate system alkalinity = 2 - 0.13 = 1.87 meq/l

Detergent carbonate concentration = 1.3 kg/cap.-yr. at 150 gal/cap.-day

Detergent carbonate alkalinity =

$$\frac{6.5\text{mg}}{l} \times \frac{2\text{meq}}{\text{mM}} \times \frac{1}{100\ \text{mg}} = 0.123\ \text{meq/l}$$

So total alkalinity = 1.87 + 0.123 = 1.993, or approx. 2.0 meq/l

= 100 mg $CaCO_3/l$

Thus, even if Na_2CO_3 were to fully replace detergent P, there would be no significant change in the total alkalinity of the wastewater. Further, since the detergent P contributes an alkalinity of only 0.13 meq/l or 6.5 mg $CaCO_3/l$, partial (50% replacement) or excess (150% replacement) of detergent P alkalinity by Na_2CO_3 alkalinity would only change the alkalinity by approximately 3-4 mg $CaCO_3/l$. Again, even at a low alkalinity (100 mg $CaCO_3/l$) this change is negligible.

DEVELOPMENT OF THE MODEL

Several modifications (and corrections) were made in the model calculations presented in the Ferguson (1972) paper and the Ferguson & King (1977) article. A description of the final model calculations and the program flowsheet is presented in Appendix I. A program listing and a disk containing the model calculations in FORTH also is appended (Appendix II). The FORTH programming language was used because its speed and compactness make it suited for microcomputers.

The model was developed in as general a form as possible, to increase its flexibility. The stoichiometry of the aluminum phosphate or ferric phosphate precipitate can be varied. In the Ferguson and King (1977) model, the aluminum phosphate solid stoichiometry was $Al_{1.4}PO_4(OH)_{1.2(s)}$ with a solubility product of $K_{so} = 10^{-34}$ -- a value that produced agreement between model predictions and laboratory jar test and pilot plant results for P residual. In the data presented in this report, the stoichiometry of $Al_{1.5}PO_4(OH)_{1.5(s)}$ is used, since this appeared to provide a reasonable agreement with available field scale and pilot scale data on simultaneous precipitation/biological treatment. The stoichiometry chosen for the work with ferric phosphate precipitation was $Fe_{1.2}PO_4(OH)_{0.6(s)}$. This value, and the associated solubility product of $K_{so} = 10^{-36.3}$ was chosen so that the predicted data would fit the observations of Recht and Ghassemi (1970). Again, as noted for the aluminum phosphate model, this stoichiometry can be varied.

Experiments
-> 1.4

The Ferguson and King (1977) model was found to contain a discontinuity in the P residual calculation section between the one precipitate and two precipitate cases. Because the formation of one precipitate -- the metal phosphate -- at doses of metal ion less than the stoichiometric requirement is an experimentally observed phenomenon, it was decided to handle the calculation discontinuity by manual extrapolation across the boundary between the two cases.

A typical example of this extrapolation technique is presented in Figure 1. In general, the extent of extrapolation required was greater for any given set of conditions for ferric phosphate precipitation by ferric chloride than for aluminum phosphate precipitation using alum (Figures 1 and 2).

The degree of extrapolation required also increased with increasing initial pH and alkalinity, and with decreasing initial phosphate. In the Ferguson & King (1977) paper, only two cases were used to determine how the model behaved for alum -- these were a very low alkalinity (75 mg as $CaCO_3/l$) and a very high alkalinity (400 mg as $CaCO_3/l$). Both of the cases used the rather high pH (for simultaneous precipitation) of 8.5. Under these conditions and using hand calculations, two types of phosphate-residual-versus-alum-dose curves were obtained. (See Figure 3, which is a copy of Figure 9 of the Ferguson and King (1977) paper).

Figures 4 and 5 show a comparison between the Ferguson and King (1977) figures and the predictions of the current model. For low alkalinity (75 mg $CaCO_3/l$) there is excellent agreement between the simulations of Ferguson & King (1977) and the model predictions (Figure 4). At high alkalinity (400 mg $CaCO_3/l$) the discontinuity between the one- and the two-precipitate regimes is evident, and there is less agreement with the simulations of Ferguson & King (1977) (Figure 5). Extrapolations such as those used fo the model outputs discussed later do however fit the Ferguson & King (1977) data in the region between

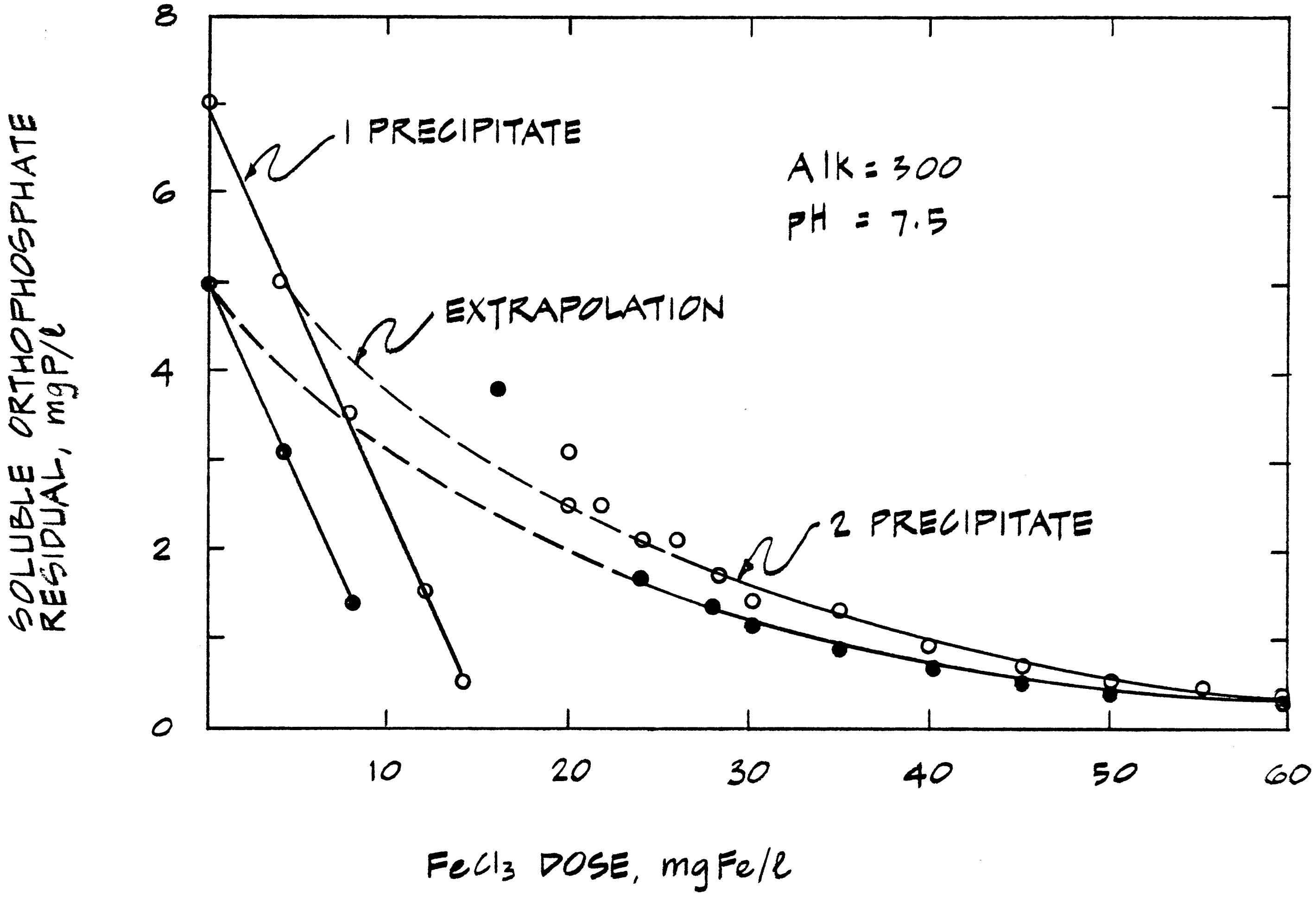


FIGURE 1 Example of Extrapolation Between One and Two Ppt Cases ($FeCl_3$ dosing)

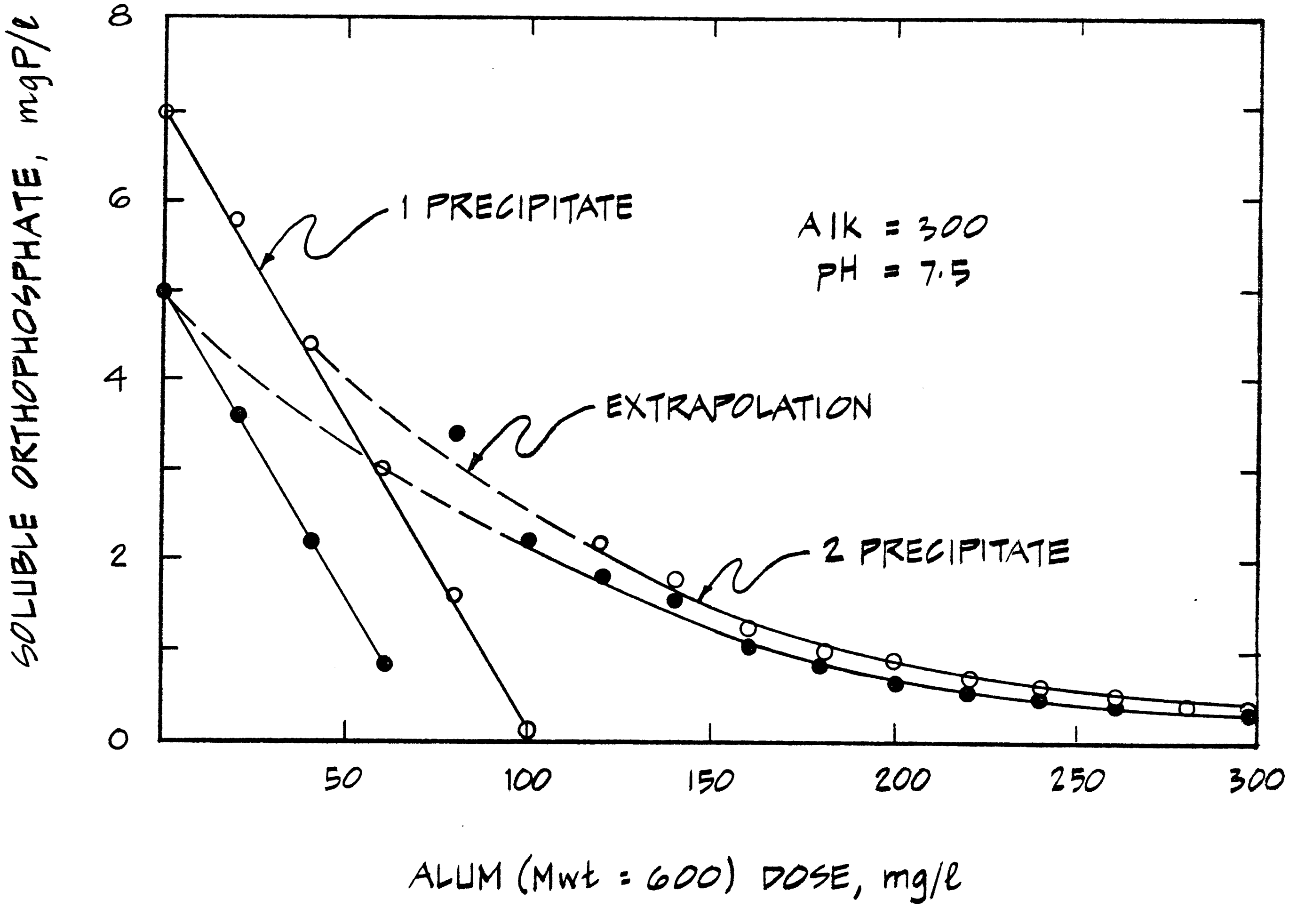


FIGURE 2 Example of Extrapolation Between One and Two Ppt. Cases (Alum Dosing)

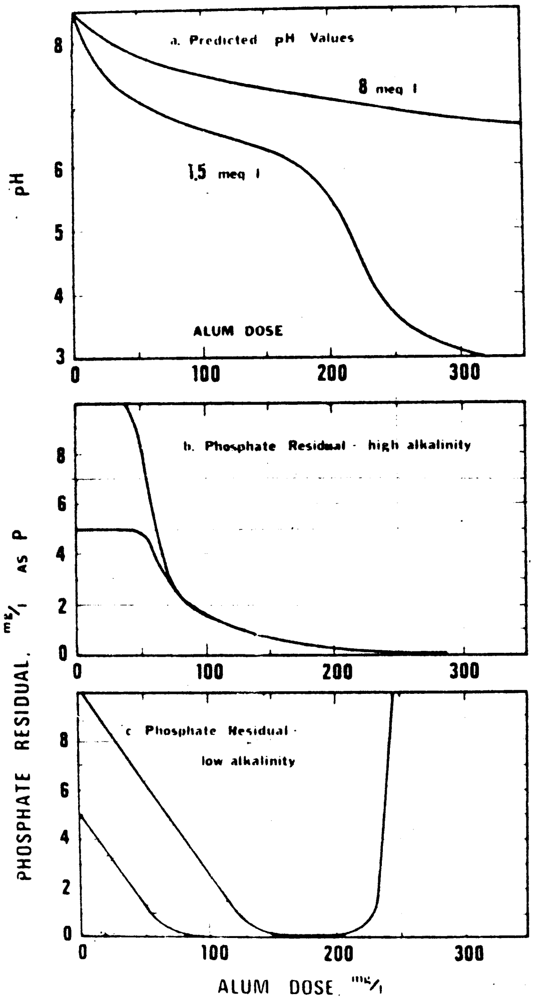


FIGURE 9. Simulation for high and low alkalinity wastewater (pH 8.5) for initial phosphate concentrations of 5 and 10 mg/l as P. (13a) Wastewater pH versus alum dosage for 10 mg/l initial phosphorus; (13b) Phosphate residuals for high alkalinity (8 meq/l) wastewater; (13c) Phosphate residuals for low alkalinity (1.5 meq/l) wastewater.

FIGURE 3 Ferguson and King (1977) Simulations of Phosphate Residual and pH for Alum Dosing. Conditions indicated in Figure caption.

FIGURE 4 Ferguson and King Simulation and Model Predictions for Low Alkalinity Case

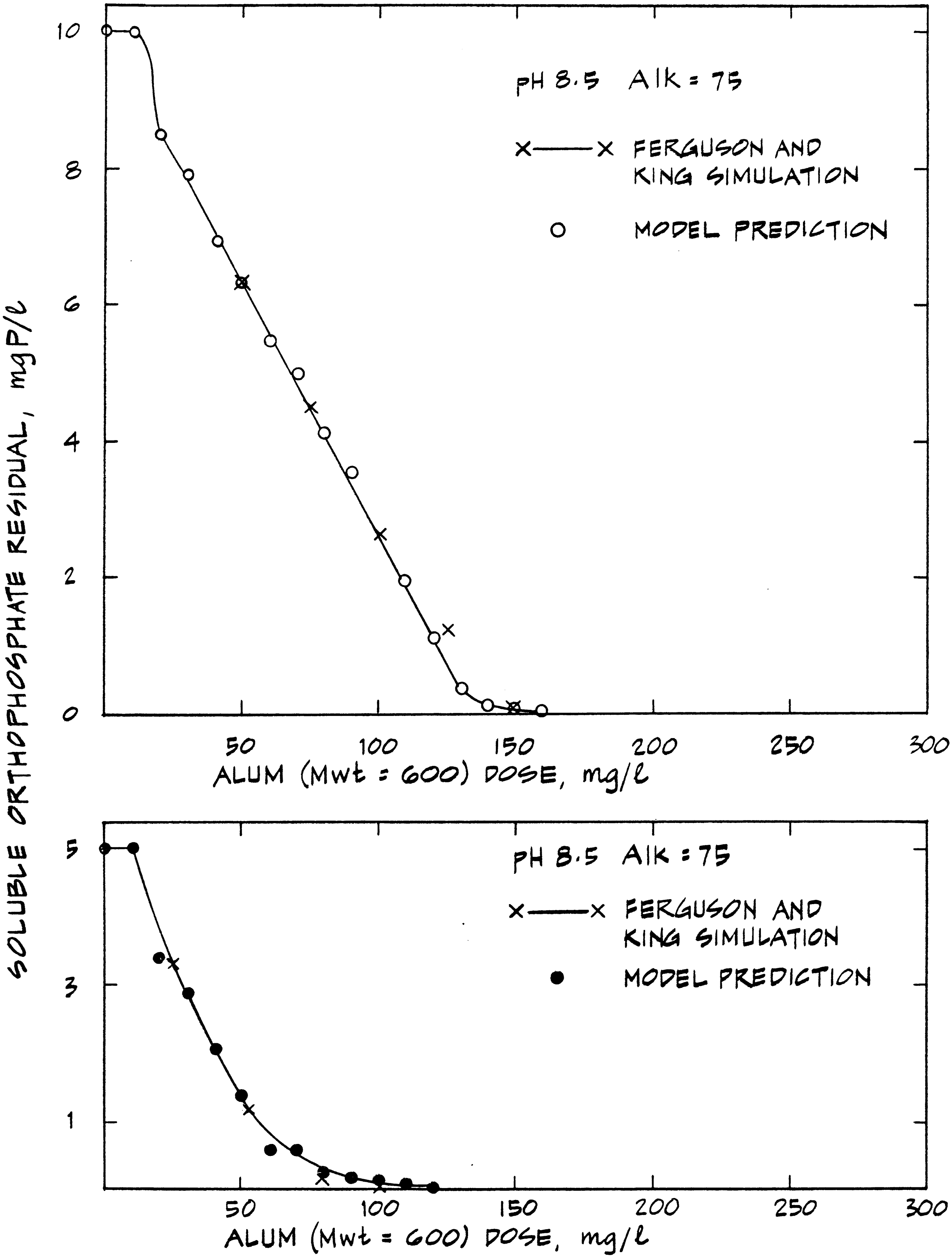
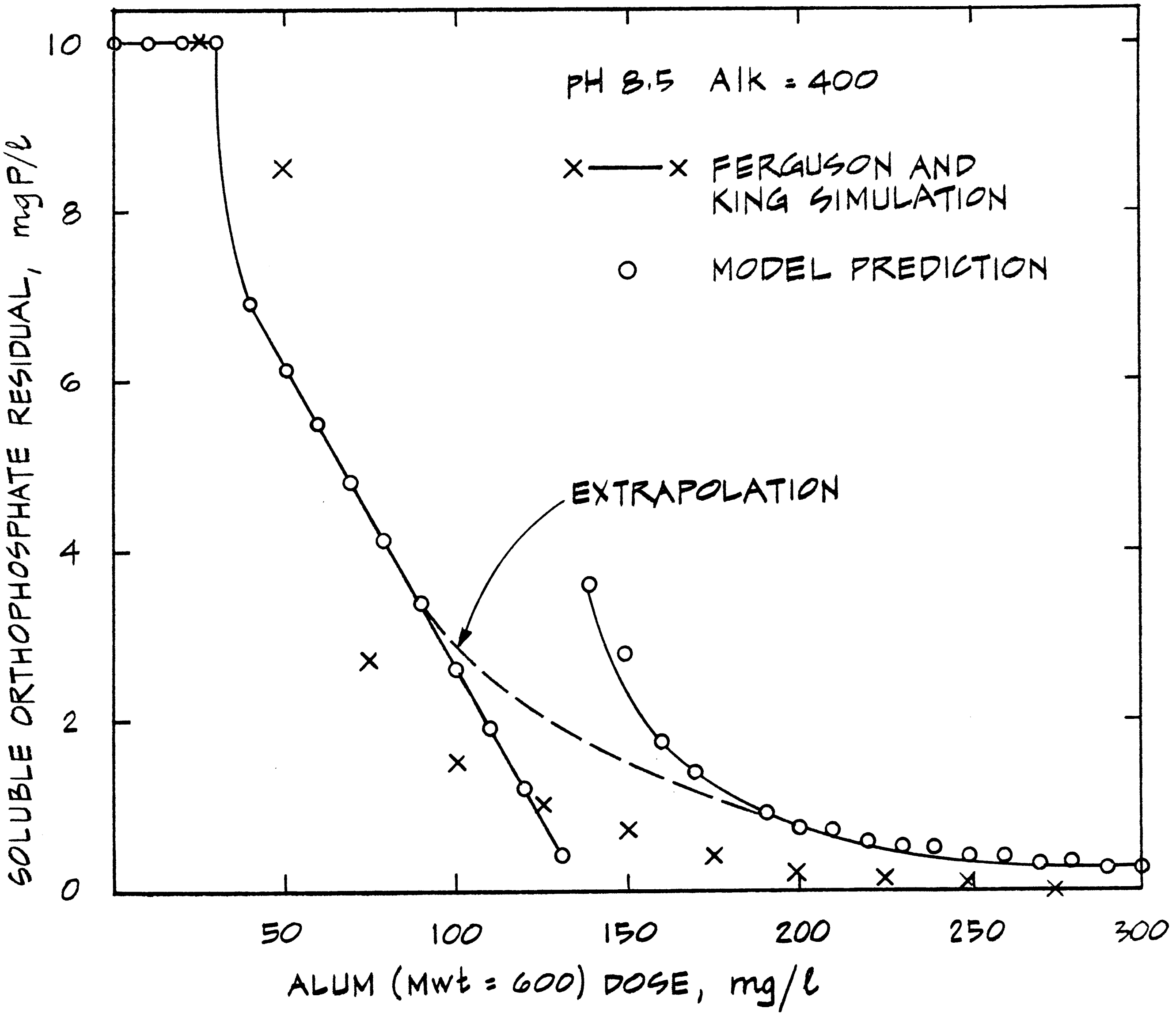
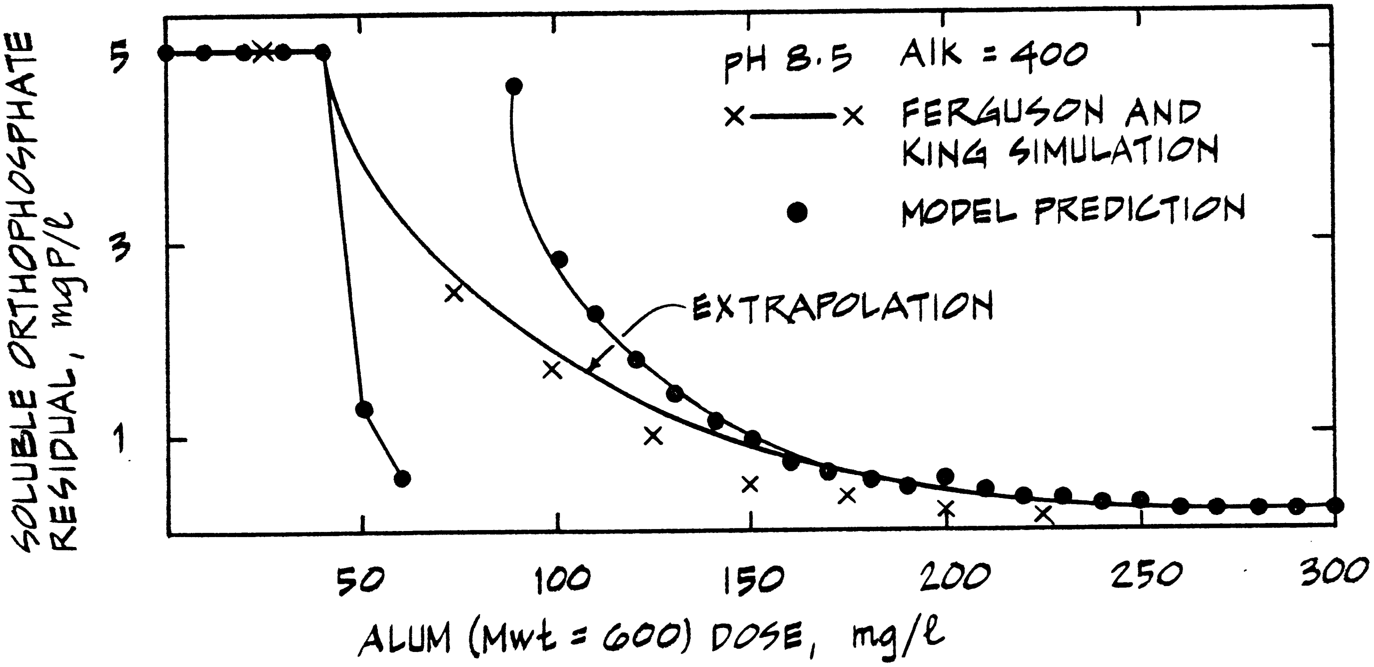


FIGURE 5 Ferguson and King Simulation and Model Prediction for High Alkalinity Case





the one- and two-precipitate regimes. It is possible that the hand calculation used by Ferguson & King (1977) was not discriminating enough to detect the discontinuity in the high alkalinity cases.

The existence of a discontinuity in the model predictions can present a dilemma in extrapolation, because in some cases, especially at high pH (7.5), high alkalinity (200-300 mg as $CaCO_3/l$), and low initial P concentration, the results might be extrapolated in two different ways. Figure 3 illustrates this dilemma. There is support for the existence of the curves produced by methods of extrapolation (Ferguson & King, 1977).

It is not known which extrapolation (or either) between the one- and two-precipitate cases correctly describes the actual operating situation in the region of the extrapolations. The impact of making one or another of the two types of extrapolation on the change in chemical dose for a given change in influent soluble ortho-P (and therefore on the treatment cost for detergent phosphate) will be discussed in the results section. In general, the impact is negligible below soluble ortho-P residuals of 0.5 mg P/l. It becomes more and more evident as the desired soluble ortho-P residual increases above this value.

RESULTS OF MODEL PREDICTIONS

As previously mentioned, the model was used to predict the soluble ortho-P residuals obtained by dosing either ferric ion (as ferric chloride) or aluminium ion (as alum) to solutions with the following ranges of composition:

- initial soluble ortho-P concentrations of 7, 5, 4, 3, and 2.5 mg P/l
- initial alkalinities of 100, 200, and 300 mg $CaCO_3$/l
- initial pH values of 7 and 7.5

The model determined the chemical doses required to achieve dissolved ortho-P residuals of 1.5, 1.1, 0.8, 0.5, 0.3 and 0.1 mg P/l.

The general technique was to enter the initial composition (pH, soluble ortho-P and total alkalinity), and then to run the computer program to print out soluble ortho-P residuals at various chemical doses. These results then were hand-plotted, and extrapolations were made if needed in the region between the one- and the two-precipitate cases (if necessary by both of the extrapolation methods indicated previously). The curves for all of the cases examined are provided in Appendix III.

Tables 3 through 6 summarize the doses of either $FeCl_3$ (as Fe) or alum (as alum, with molecular weight = 600) required to reach the indicated soluble ortho-P residual. The data are for the "smooth curve" type of extrapolation (extrapolation 1). Where the shoulder type of extrapolation (extrapolation 2) also was used, the results are presented in parentheses.

Tables 7 through 10 present the final pH values that correspond to the chemical doses in Tables 3 through 6. From these data it would appear that, from a pH standpoint, all but some of the 0.1 mg P/l soluble

Table 3. $FeCl_3$ doses (as mg Fe/l) to achieve indicated soluble orthophosphate residual; initial pH 7.

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5		
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
Residual soluble orthophosphate, mg P/l															
1.5	12	13.5	15.5	7.5	10.5	12.5	6	8.5	10(11)	4	5(8)	9.5	4	6(7)	8(9)
1.1	13.5	16.0	19.5	9.5	13	17	8.5	13	17	7	9.5(10.5)	16.5	7	10.5	16.5
0.8	15.5	19	26	12	16.5	23	11	18	25	10	15	25	10	15.5	24
0.5	18.5	25.5	35	16	20	35	15	25	37	14	25	34	14	25	35
0.3	21.5	35	50	20	35	50	20	35	53	19	37	48	18	36	50
0.1	32	55	--	32	55	--	30	52	--	30	53	--	29	53	--

Table 4. $FeCl_3$ doses (as mg Fe/l) to achieve indicated soluble orthophosphate residual; initial pH 7.5.

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5		
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
Residual soluble orthophosphate, mg P/l															
1.5	15(15.5)	22.5	30.5	12(13.5)	18.5	25.5	7.5(13)	14(18.5)	22.5(26)	3.5(10.5)	12(18)	17(24.5)	5.5(9.5)	10(16.5)	16(24)
1.1	17.5	25.5	36.5	15(15.5)	22.5	31	11(14.5)	20(23)	31(32)	8.5(12)	18(21)	25.5(30)	9(12)	16.5(21)	26.5(29)
0.8	20	30	43	17.5	26	37	15(16)	26(28)	38	12(15)	24.5(25)	34(36)	12.5(14.5)	23(25)	35
0.5	23.5	36	50	20.5	32	45	20	35	47	17.5(18.5)	32.5	45.5	17.5(18)	31.5(32)	45.5
0.3	27.5	47.5	60	23.5	40	55	24	42	60	23	42.5	60	22	40	60
0.1	36	55?	--	29	52	--	32	60	--	31	60	--	30	60	--

Table 5. Alum doses (as mg/l alum, mwt = 600) to achieve indicated soluble orthophosphate residual; initial pH 7.

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5		
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
Residual soluble orthophosphate, mg P/l															
1.5	80	80	84	50	56	65	35	37	55	22(25)	25(32)	47	15(20)	20(25)	32(40)
1.1	87	94	102	58	67	92	42	57	82	30(37)	47(55)	77	25(32)	45(53)	70
0.8	95	108	135	68	87	125	55	82	120	42(47)	77(80)	115	40(45)	77	110
0.5	107	125	200	81	135	180	75	127	180	65	122	170	67	127	170
0.3	120	190	250	105	190	250	100	175	255	95	175	245	100	180	250
0.1	150	280	--	150	280	--	150	285	--	155	285	--	150	285	--

Table 6. Alum doses (as mg/l alum, mwt=600) to achieve indicated soluble orthophosphate residual; initial pH 7.5.

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5		
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300
Residual soluble orthophosphate, mg P/l															
1.5	83	120	147	60(67)	100	132	47(55)	67(90)	100(120)	27(53)	60(90)	95(117)	30(50)	55(80)	78(113)
1.1	95	135	170	75(77)	120	157	62(67)	97(110)	137(143)	45(63)	87(105)	135(145)	45(57)	85(97)	123(140)
0.8	105	155	200	89	140	185	77(80)	127(132)	170	62(73)	117(125)	175(177)	62(67)	117(123)	165(173)
0.5	120	190	260	107	170	275	97	170	235	90	160	235	87	160	225
0.3	140	260	--	130	260	290	120	225	300	112	205	300	110	210	300
0.1	180	300	--	180	300	--	175	--	--	170	300	--	170	300	--

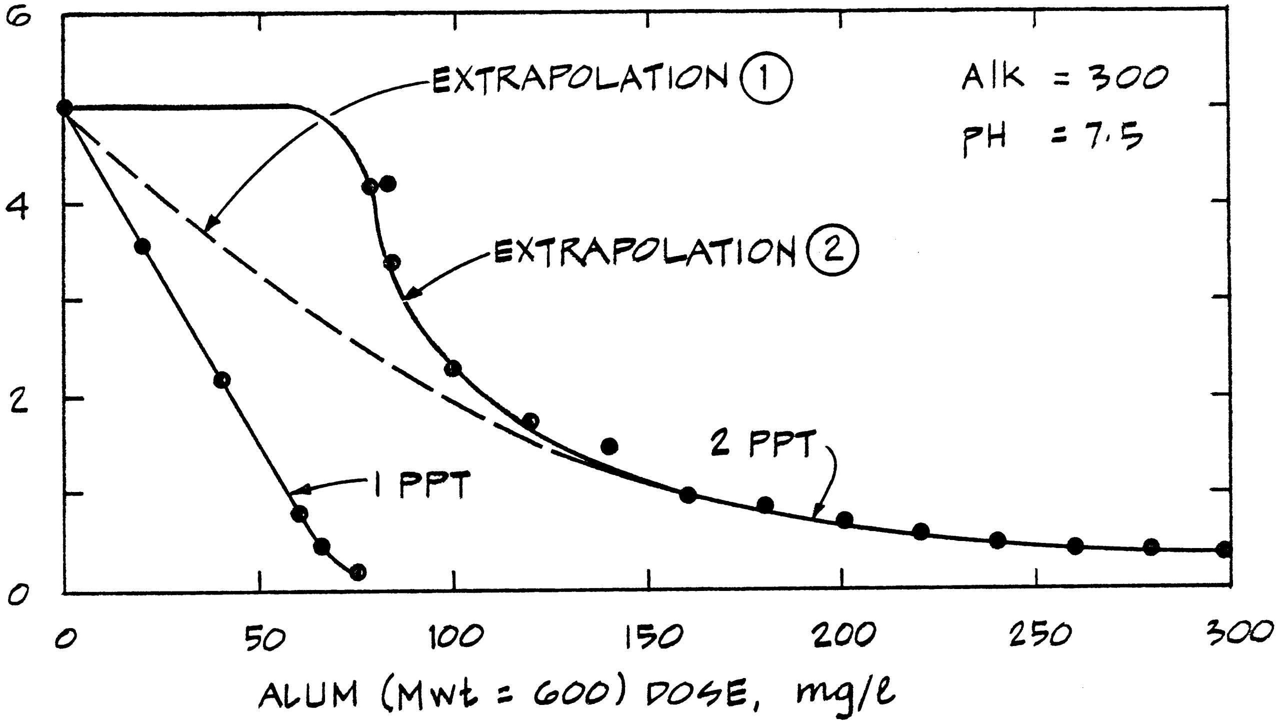


FIGURE 6 The Two Types of Extrapolation Possible in the Region of Discontinuity Between One and Two Precipitate Cases

Table 7. Final pH values corresponding to $FeCl_3$ doses in Table 3 (initial pH 7).

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5			
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	
Residual soluble orthophosphate, mg P/l																
1.5	6.7	6.8	6.8	6.9	6.8	6.9	6.8	6.9	6.9	6.9	6.9	6.8	6.8	6.9	6.9	6.85
1.1	6.6	6.8	6.7	6.7	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.77
0.8	6.5	6.6	6.7	6.6	6.7	6.7	6.7	6.6	6.7	6.7	6.7	6.7	6.7	6.6	6.7	6.6
0.5	6.5	6.6	6.5	6.5	6.7	6.5	6.5	6.5	6.5	6.5	6.5	6.4	6.4	6.5	6.5	6.51
0.3	6.4	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.31
0.1	5.9	6.0	--	5.8	5.9	--	5.8	6.0	--	5.8	5.9	--	5.8	5.9	--	5.88

Table 8. Final pH values corresponding to $FeCl_3$ doses in Table 4 (initial pH 7.5).

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5			
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	
Residual soluble orthophosphate, mg P/l																
1.5	6.9	6.9	6.8	7.0	6.9	6.9	7.2	7.0	6.9	7.3	7.1	7.1	7.2	7.1	7.1	7.03
1.1	6.8	6.8	6.7	6.8	6.8	6.8	7.0	6.8	6.8	7.0	6.9	6.8	6.9	6.9	6.8	6.84
0.8	6.7	6.7	6.6	6.7	6.7	6.7	6.7	6.7	6.6	6.8	6.7	6.7	6.7	6.7	6.7	6.69
0.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
0.3	6.3	6.3	6.3	6.4	6.3	6.4	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.31
0.1	5.8	6.1	--	6.1	6.1	--	5.8	5.8	--	5.8	5.8	--	5.9	5.8	--	5.9

Used ?

Table 9. Final pH values corresponding to alum doses in Table 5 (initial pH 7).

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5			
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	
Residual soluble orthophosphate, mg P/l																
1.5	6.5	6.8	6.8	6.7	6.8	6.8	6.8	6.9	6.9	6.8	6.9	6.9	6.9	6.9	6.9	6.84
1.1	6.5	6.7	6.8	6.7	6.7	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.76
0.8	6.5	6.7	6.7	6.6	6.7	6.7	6.7	6.7	6.7	6.8	6.7	6.7	6.7	6.7	6.7	6.69
0.5	6.4	6.6	6.5	6.5	6.6	6.5	6.5	6.5	6.5	6.6	6.5	6.5	6.6	6.5	6.5	6.52
0.3	6.3	6.4	6.4	6.4	6.3	6.4	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.33
0.1	6.1	6.0	--.	6.0	6.0	--	6.0	5.9	--	5.9	5.9	--	5.9	5.9	--	5.96

Table 10. Final pH values corresponding to alum doses in Table 6 (initial pH 7.5).

Initial soluble orthophosphate mg P/l	7			5			4			3			2.5			
Alkalinity mg $CaCO_3$/l	100	200	300	100	200	300	100	200	300	100	200	300	100	200	300	
Residual soluble orthophosphate, mg P/l																
1.5	6.8	6.9	6.9	7.0	6.9	6.9	7.1	7.1	7.0	7.3	7.1	7.0	7.2	7.1	7.1	7.03
1.1	6.8	6.8	6.8	6.8	6.8	6.8	6.9	6.9	6.9	7.0	6.9	6.8	7.0	6.9	6.9	6.87
0.8	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.8	6.7	6.7	6.8	6.7	6.7	6.71
0.5	6.5	6.5	6.5	6.5	6.6	6.6	6.6	6.5	6.6	6.5	6.5	6.5	6.6	6.5	6.5	6.53
0.3	6.3	6.2	--	6.3	6.2	6.4	6.3	6.3	6.3	6.3	6.4	6.3	6.3	6.3	6.3	6.3
0.1	6.0	6.0	--	5.8	6.0	--	5.8	--	--	5.8	5.9	--	5.8	5.9	--	5.89

ortho-P residuals could be achieved consistent with biological treatment (i.e. using simultaneous precipitation). There are other process factors that may prevent this. To illustrate this point, the averages of the pH data for four conditions ($FeCl_3$ dosing with initial pH values of 7 and 7.5, and alum dosing with initial pH values of 7 and 7.5) are plotted in Figure 7 against soluble residual ortho-P. From this plot it appears that pH values consistent with biological treatment (≥ 6.2) will be maintained for soluble ortho-P residuals of 0.25 mg P/l.

Using the $FeCl_3$ and alum dose data from Tables 3 through 6, it was possible to compute the reduction in chemical dose that would result from the influent P reductions due to a detergent p ban. This was done for each soluble ortho-P residual, initial pH and alkalinity; the results are presented in Tables 11 through 16. These data are also summarized graphically in Figures 8 and 9. Two things emerge from these Figures. First, for any given P residual there is a considerable range of chemical dose reductions for a given influent P reduction. Second, as the required soluble ortho-P residual decreases, the chemical dose reduction attributable to a decrease in influent P decreases. In Figures 8 and 9 the average chemical dose reductions are presented for both methods of extrapoltion. With either method of extrapolation the same general average trend of decreasing "savings" in chemical dose for reductions in influent dissolved ortho-P is shown. The differences in the predictions given by the two methods of extrapolation increases as the dissolved ortho-P residual increases. In general the difference is minor for dissolved ortho-P residuals of below 0.5 mg P/l and becomes significant for

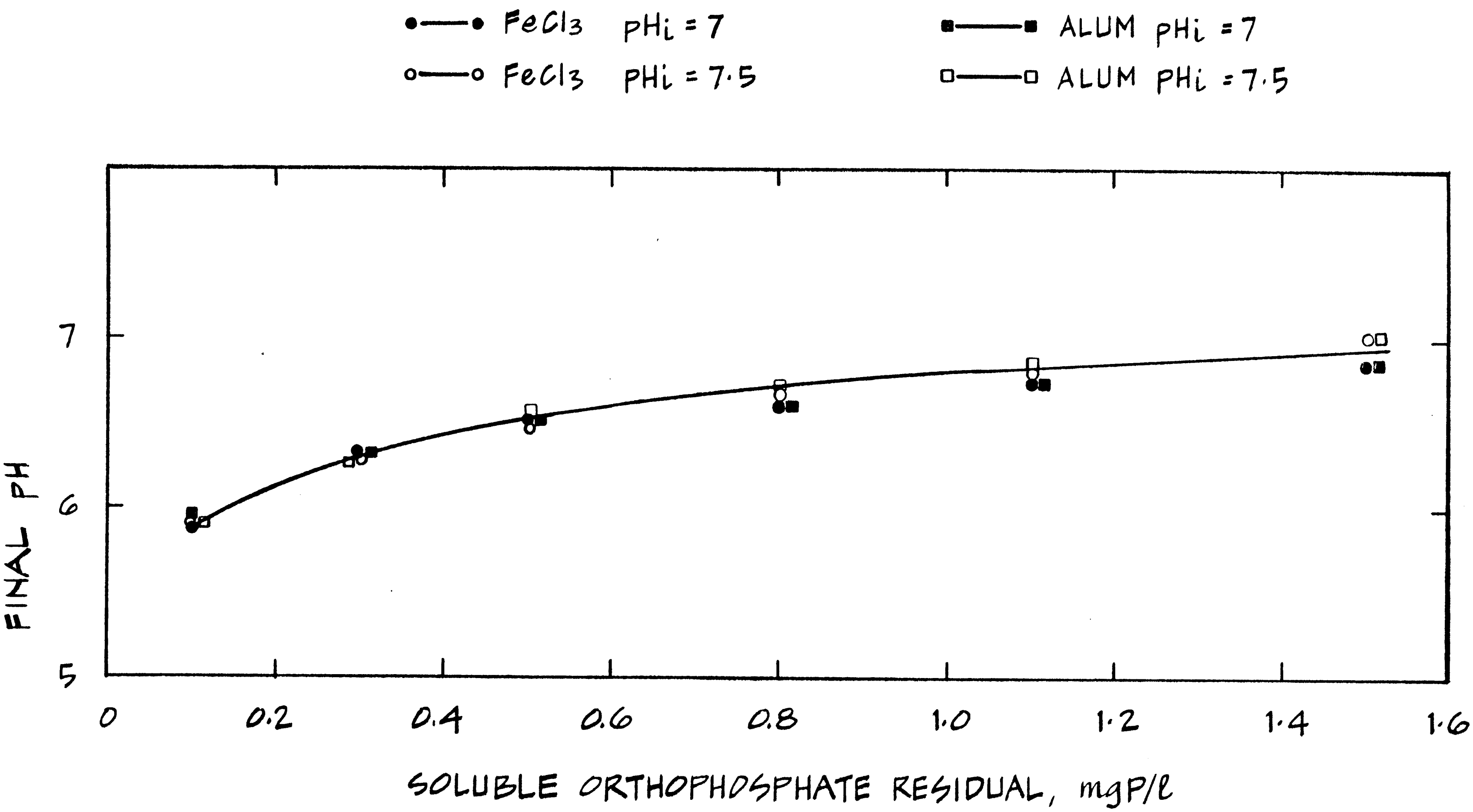


FIGURE 7 Final pH for Various Soluble Orthophosphate Residuals for both $FeCl_3$ and Alum Dosing

TABLE 11 Reductions in $FeCl_3$ Dose for a Reduction in Influent Soluble Orthophosphate from 7 to 5 mg P/l. Figures are (Δ moles $FeCl_3$)/(Δ moles P).

Soluble Residual Orthophosphate,	pH 7 Alkalinity, mg $CaCO_3$/l			pH 7.5 Alkalinity, mg $CaCO_3$/l		
mg P/l	100	200	300	100	200	300
1.5	1.2	0.83	0.83	0.83 (0.55)	1.1	1.4
1.1	1.1	0.83	0.69	0.69 (0.55)	0.83	1.5
0.8	1.2	0.69	0.83	0.69	1.1	1.7
0.5	0.69	1.5	0.0	0.97	1.1	1.4
0.3	0.42	0.0	0.0	1.1	2.1	1.4
0.1	0.0	—	—	1.9	0.83	—

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

TABLE 12 Reductions in $FeCl_3$ Dose for a Reduction in Influent Soluble Orthophosphate from 5 to 3 mg P/l. Figures are (Δ moles $FeCl_3$)/(Δ moles P).

Soluble Residual Orthophosphate, mg P/l	pH 7			pH 7.5		
	Alkalinity, mg $CaCO_3$/l			Alkalinity, mg $CaCO_3$/l		
	100	200	300	100	200	300
1.5	0.97	1.5 (0.69)	0.83	1.8 (0.83)	1.8 (0.14)	2.4 (0.28)
1.1	0.69	0.97 (0.69)	0.14	1.8 (0.97)	1.2 (0.41)	1.5 (0.28)
0.8	0.55	0.42	0.55	1.5 (0.69)	0.42 (0.28)	0.83 (0.28)
0.5	0.55	1.4	0.28	0.83 (0.41)	0.14	0.14
0.3	0.28	0.55	0.55	0.14	0.69	0.14
— 0.1	0.55	0.0	—	0.55	—	—

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

TABLE 13 Reductions in $FeCl_3$ Dose for a Reduction in Influent Soluble Orthophosphate from 4 to 2.5 mg P/l. Figures are (Δ moles $FeCl_3$)/(Δ moles P).

Soluble Residual Orthophosphate, mg P/l	pH 7 Alkalinity, mg $CaCO_3$/l			pH 7.5 Alkalinity, mg $CaCO_3$/l		
	100	200	300	100	200	300
1.5	0.73	0.92	0.73	0.73 (1.3)	1.5 (0.73)	2.4 (0.73)
1.1	0.55	0.92	0.18	0.73 (0.93)	1.7 (0.73)	1.7 (1.1)
0.8	0.37	0.92	0.37	0.92 (0.55)	1.1 (1.1)	1.1
0.5	0.37	0.0	0.74	0.92 (0.73)	1.3	0.55
0.3	0.74	0.0	1.1	0.73	0.74	0.0
0.1	0.37	—	—	0.73	0.0	—

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

TABLE 14 Reductions in Alum Dose for a Reduction in Influent Soluble Orthophosphate from 7 to 5 mg P/l. Figures are (Δmoles Al)/(Δmoles P).

Soluble Residual Orthophosphate, mg P/l	pH 7 Alkalinity, mg $CaCO_3$/l			pH 7.5 Alkalinity, mg $CaCO_3$/l		
	100	200	300	100	200	300
1.5	1.6	1.2	0.98	1.2 (0.83)	1.0	0.78
1.1	1.5 (0.93)	1.4	0.52	1.93	0.78	0.67
0.8	1.4	1.1	0.52	0.83	0.78	0.78
0.5	1.3	0.0	1.0	0.67	1.0	1.8
0.3	0.78	0.0	0.0	0.52	0.0	—
0.1	0.0	0.0	—	0.0	0.0	—

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

TABLE 15 Reductions in Alum Dose for a Reduction in Influent Soluble Orthophosphate from 5 to 3 mg P/l. Figures are (Δ moles Al)/(Δ moles P).

Soluble Residual Orthophosphate, mg P/l	pH 7 Alkalinity, mg $CaCO_3$/l			pH 7.5 Alkalinity, mg $CaCO_3$/l		
	100	200	300	100	200	300
1.5	1.4 (1.3)	1.6 (1.2)	0.93	1.7 (0.72)	2.1 (0.52)	1.9 (0.78)
1.1	1.5 (1.1)	1.0 (0.62)	0.78	1.6 (0.72)	1.7 (0.78)	1.1 (0.67)
0.8	1.3 (1.1)	0.52 (0.36)	0.52	1.4 (0.83)	1.2 (0.78)	0.52
0.5	0.83	0.67	0.52	0.88	0.52	0.52
0.3	0.52	0.78	0.26	0.93	0.0	0.0
0.1	0.26	0.26	0.0	0.52	0.0	—

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

TABLE 16 Reductions in Alum Dose for a Reduction in Influent Soluble Orthophosphate from 4 to 2.5 mg P/l. Figures are (Δmoles Al)/(Δmoles P).

Soluble Residual Orthophosphate, mg P/l	pH 7			pH 7.5		
	Alkalinity, mg $CaCO_3$/l			Alkalinity, mg $CaCO_3$/l		
	100	200	300	100	200	300
1.5	1.4 (1.0)	1.2 (0.82)	1.6 (1.0)	1.2 (0.34)	0.82 (0.69)	1.5 (0.48)
1.1	1.2 (0.69)	0.83 (0.28)	0.83	1.2 (0.69)	0.83 (0.90)	0.96 (0.21)
0.8	1.0 (0.69)	0.34	0.69	1.0 (0.89)	0.69 (0.62)	0.34 (0.21)
0.5	0.55	0.34	0.69	0.69	0.69	0.69
0.3	0.0	0.0	0.34	0.69	1.03	0.0
0.1	0.0	0.0		0.34		

NOTE: Figures in parentheses are for the shoulder type of extrapolation.

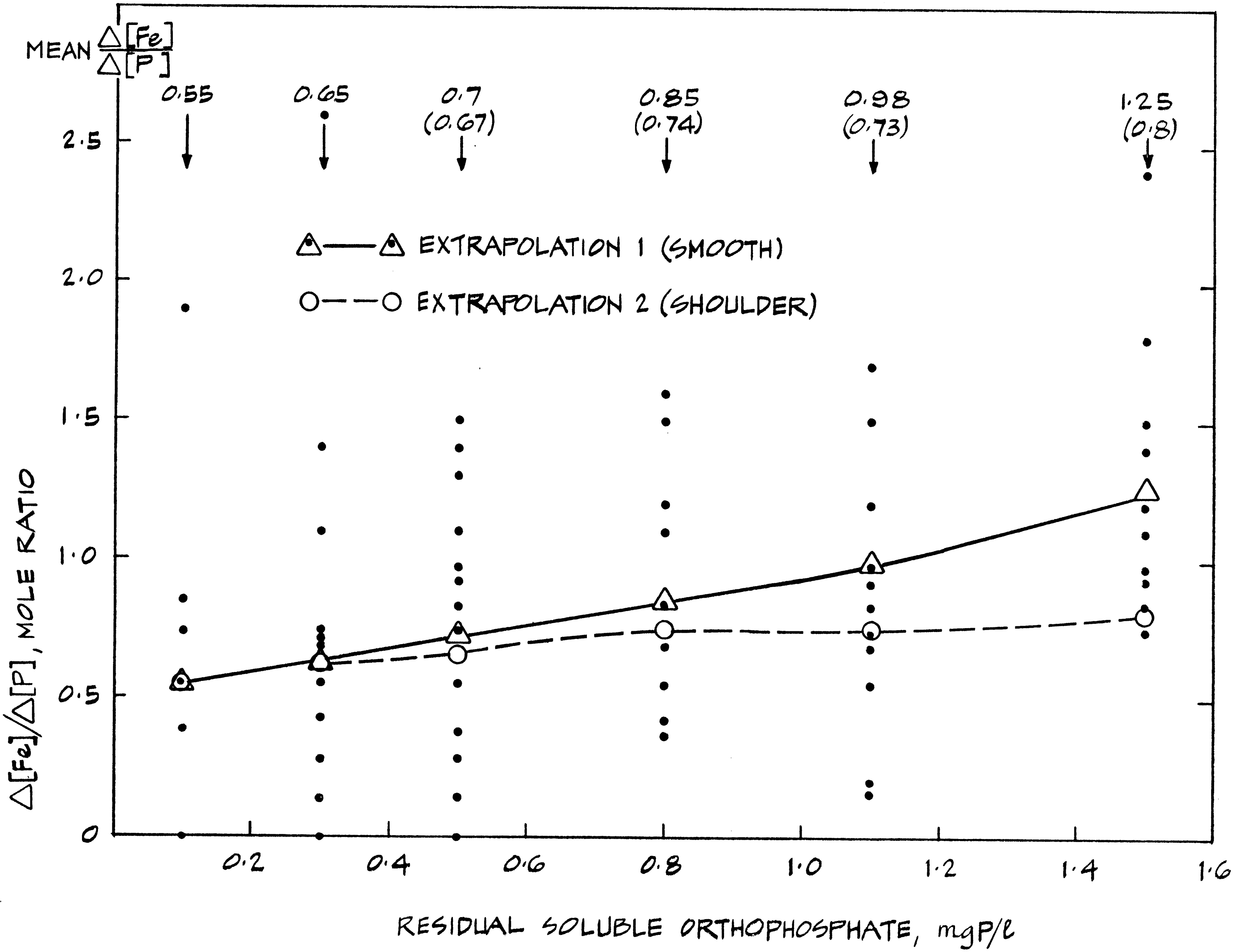


FIGURE 8 Range and Average Reduction of Iron Dose Caused by Influent Phosphate Reduction

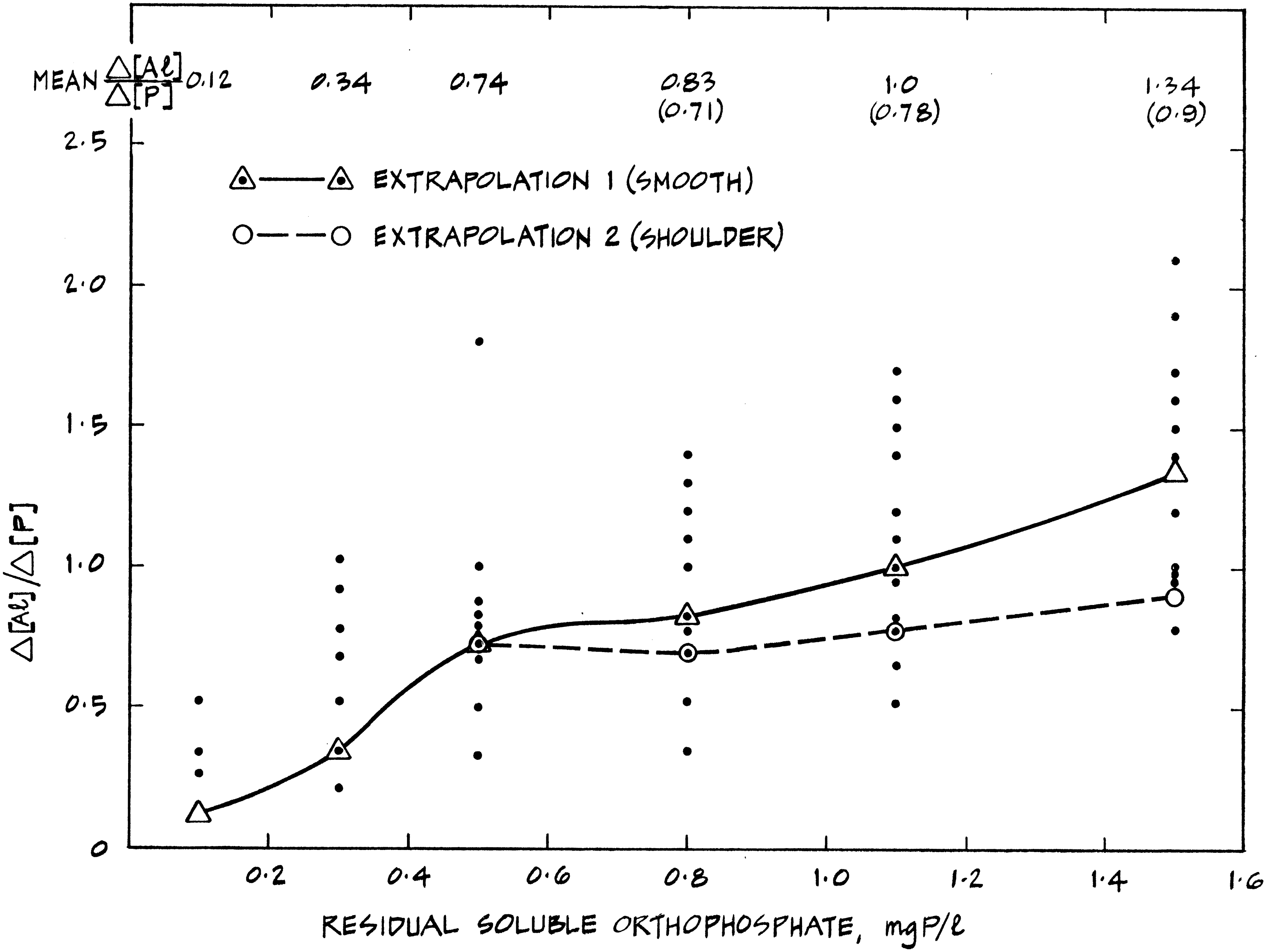


FIGURE 9 Range and Average Reduction of Alum Dose Caused by Influent Phosphate Reduction

dissolved ortho-P residuals above 1.0 mg P/l.

The model was used to assess the potential impact of a P detergent ban on the $FeCl_3$ dose required to meet various P residual requirements in a wastewater such as that found at the Blue Plains Waste Treatment Plant. Data for primary effluent alkalinity were averages (pH = 7.1; initial alkalinity = 126 mg as $CaCO_3$/l) of those in Table 17 (Blue Plains data of Ed Jones provided by R. Sedlak, Soap & Detergent Association). The influent soluble ortho-P was assumed to be 7 mg P/l with a reduction to 5 mg P/l being assumed to result from a detergent P ban. Figure 10 and Table 18 present the chemical doses required to achieve various soluble ortho-P residuals. The difference in $FeCl_3$ dose for this reduction in influent P is presented in Table 19. From this it can be seen that for a residual dissolved ortho-P of 1.5 mg P/l, the savings in $FeCl_3$ is predicted to be 4.7 lb $FeCl_3$/lb P.

DOSING WITH METAL SALTS COMBINED WITH STRONG ACID

When iron chloride, iron sulfate, or alum are added to wastewater to precipitate P, reactions also occur between these salts and the wastewater alkalinity (bicarbonate). This "side reaction" consumes chemical and may produce a hydroxide precipitate, both of which are undesirable from a treatment point of view because they result in chemical consumption and in sludge production.

In these "side reactions" the iron and aluminum ions act as strong acids, titrating the alkalinity. It is possible that chemical costs and sludge production could both be reduced if a strong acid (e.g.

TABLE 17 Blue Plains Sewage Treatment Plant East Primary, Total Alkalinity and pH Data Provided by R. Sedlak, Soap and Detergent Association

Month - Year	Mean Alkalinity	Mean pH
3 - 80	112	7.0
4	111	6.9
5	115	7.0
6	127	7.0
7	132	7.1
8	135	7.0
9	133	7.0
10	143	7.3
11	148	7.2
12	121	7.1
1 - 81	151	7.2
2	101	7.1
3	106	7.1
Mean	126	7.1

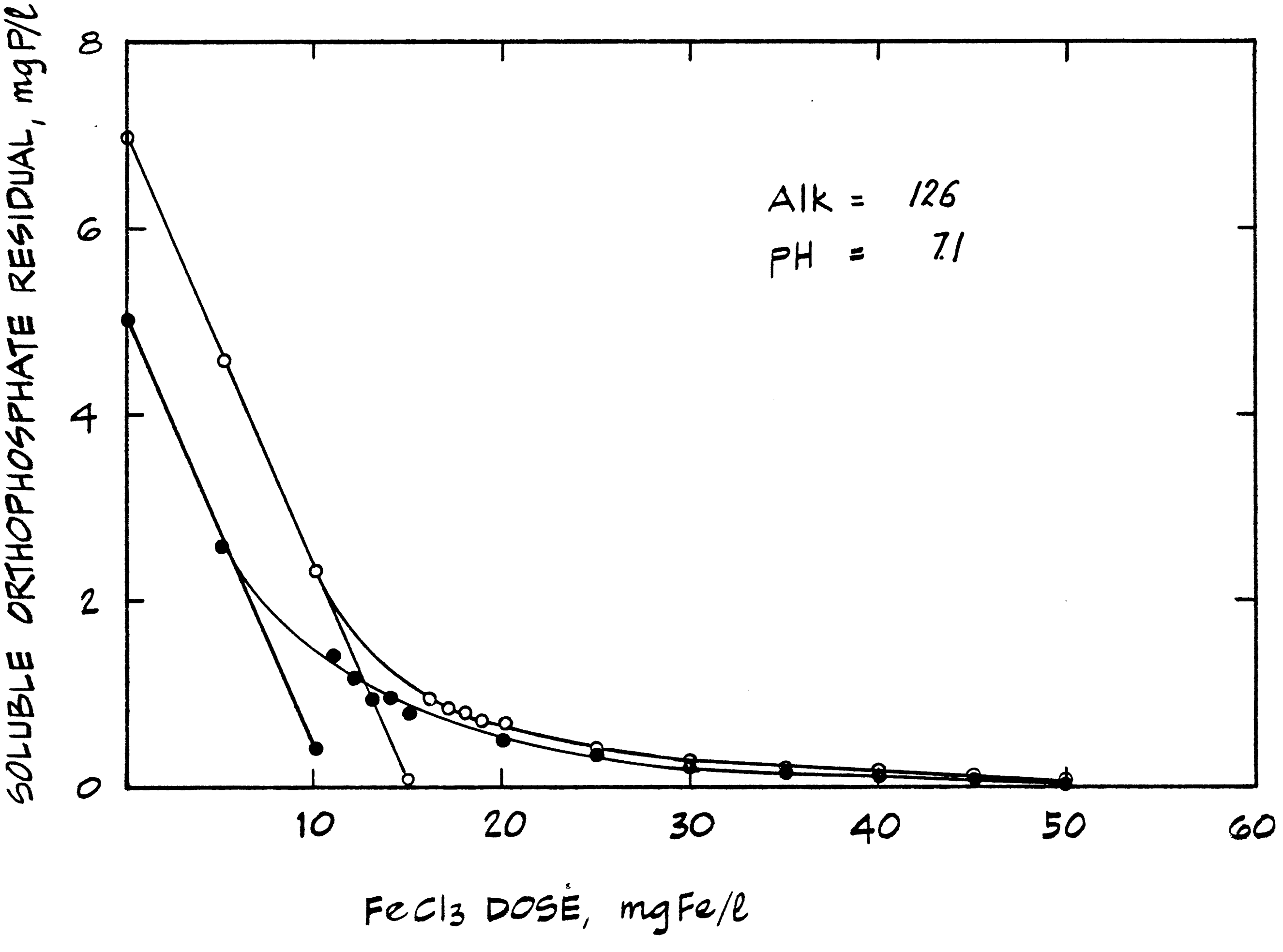


FIGURE 10 Soluble Phosphate Residual/$FeCl_3$ Dose Curves for "Blue Plains" Case; Initial pH = 7.1; Total Alkalinity = 126 mg as $CaCO_3$/l

Table 18. Ferric chloride doses required to achieve various soluble orthophosphate residuals. Blue Plains case: initial pH = 7.1; initial total alkalinity = 126 mg as $CaCO_3$/l.

Initial soluble orthophosphate concentration, mg P/l	7		5		4.2	
Residual soluble orthophosphate concentration, mg P/l	$FeCl_3$ dose mg Fe/l	$FeCl_3$ dose Mole Fe added / Mole P present	$FeCl_3$ dose mg Fe/l	$FeCl_3$ dose Mole Fe added / Mole P present	$FeCl_3$ dose Mg Fe/l	$FeCl_3$ dose Mole Fe added / Mole P present
1.5	12.5	1.0	9	1.0	8	1.1
1.1	15	1.2	12	1.3	11.5	1.5
0.8	17.5	1.4	15	1.7	14.5	1.9
0.5	22	1.7	20	2.2	20	2.6
0.3	27.5	2.2	26	2.9	25	3.3
0.1	38	3.0	38	4.2	38	5.0

TABLE 19 Predicted $FeCl_3$ Savings for an Influent P Reduction from 7 to 5 mg P/l. (Blue Plains Case)

Residual Soluble Orthophosphate Concentration mg p/l	$FeCl_3$ Savings Δmole Fe/Δmole P	Δlb $FeCl_3$ /Δlb P
1.5	0.9	4.7
1.1	0.8	4.2
0.8	0.7	3.7
0.5	0.6	3.1
0.3	0.4	2.1
0.1	0.0	0.0

sulfuric acid) were used to reduce alkalinity and pH before the addition of the P precipitating chemical. To allow the computation of these factors, the following calculation scheme is presented. This scheme allows the calculation of the changes in total alkalinity and pH that would occur upon the addition of a strong acid to a wastewater. The effect that these changes have on the iron or aluminum requirements for achieving a desired P residual can be determined by running the P precipitation model for the wastewater composition before and after acid addition.

Since simultaneous precipitation processes are assumed, the following calculations assume an "open system", that is, air being bubbled vigorously through the liquid to which acid is being added so that any CO_2 that is produced will be equilibrated with the atmosphere. The CO_2 content of the atmosphere is assumed to remain constant at the initial value prior to acid addition (determined by the production of CO_2 and its stripping in the aeration system).

For an "open" system:

$$\text{Alkalinity} = \frac{K_H}{\rho CO_2}\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+]$$

where

K_H = Henry's constant for CO_2
= $10^{-1.5}$ at 25°C
ρCO_2 = partial pressure of CO_2
α values = fraction of various "carbonate" species

α_0 = H_2CO_3/total inorganic carbon

α_1 = HCO_3^-/total inorganic carbon

α_2 = CO_3-2/total inorganic carbon

K_W = equilibrium constant for water

= 10^{-14} at 25 C

For the pH range of interest (6-9)

$$\frac{K_w}{[H^+]}, [H^+], \text{ and } \alpha_2 \longrightarrow 0$$

Therefore, alkalinity = $K_H (pCO_2) \frac{\alpha_1}{\alpha_0}$

For initial wastewater conditions, pH and alkalinity due to the bicarbonate system are known; values can be found for α_0 and α_1 from Tables and pCO_2 can be calculated.

Now, strong acid is added (C_A moles/l); this has the effect of titrating some of the alkalinity, so that:

$$\text{Alkalinity} - C_A = K_H pCO_2 \frac{\alpha_1}{\alpha_0}$$

Using the new value of alkalinity, and keeping pCO_2 constant, the value of the ratio α_1/α_0 can be calculated. Tables of α_0 and α_1 can be examined to determine at which pH value this ratio is met. For convenience, Table 20 presents values of the α_1/α_0 ratio at pH values between 5 and 9. The pH and alkalinity of the wastewater following acid addition are now known, and can be used as new starting

Table 20. α Values for Carbonate Species

pH	α_1/α_0	pH	α_1/α_0	pH	α_1/α_0	pH	α_1/α_0
5.0	0.0445	6.0	0.49	7.0	4.43	8.0	44.5
5.1	0.0559	6.1	0.56	7.1	5.62	8.1	56.1
5.2	0.0704	6.2	0.741	7.2	7.06	8.2	70.4
5.3	0.0887	6.3	0.886	7.3	8.89	8.3	89.1
5.4	0.111	6.4	1.12	7.4	11.2	8.4	112
5.5	0.14	6.5	1.4	7.5	14.1	8.5	141
5.6	0.176	6.6	1.77	7.6	17.7	8.6	177
5.7	0.222	6.7	2.23	7.7	22.3	8.7	223
5.8	0.28	6.8	2.8	7.8	28.1	8.8	281
5.9	0.353	6.9	3.52	7.9	35.4	8.9	397
						9.0	445

conditions for the phosphate precipitation model.

CONCLUSIONS

1. The study reviewed the models available for predicting the residual dissolved ortho-P concentration as a function of iron or aluminum dose.

2. The equilibrium model of Ferguson & King (1977) for alum dosing was selected for study. The calculations required in the Ferguson & King model were programmed in FORTH so that the model could be run for a wide variety of cases on a microcomputer. The program was made flexible enough to consider a range of stoichiometries of both ferric phosphate and aluminium phosphate, so that the model could be used both for iron (e.g. ferric chloride) and aluminum (alum) dosing.

3. The Ferguson & King (1977) model was found to contain a discontinuity that apparently had not been detected by the authors of the model in their hand-performed calculations presented in the original work describing the model. This discontinuity occurred between the one- and two-precipitate cases. In some cases, especially for ferric chloride dosing and for high alkalinity, low initial dissolved ortho-P, and high initial pH, the discontinuity became significant, leading to uncertainty as to the method of extrapolation that should be used in the discontinuity region. Two methods of extrapolation were used in such cases, corresponding to the forms of the curves given in the Ferguson & King paper(1977).

4. In many of the cases cited above, the region of extrapolation (with its inherent uncertainties) corresponds to the ortho-P residual region of interest -- between 0.8 and 1.5 mg P/l.

5. Model predictions showed that the chemical savings that would accrue from a reduction in influent dissolved ortho-P varied over a wide range at all dissolved ortho-P residual values. The average savings in chemical dose decreased as the residual dissolved ortho-P concentration decreased.

6. A specific case using available data for the Blue Plains wastewater was examined. The model estimated chemical savings from a reduction in influent soluble ortho-P from 7 to 5 mg P/l at 4.7 lb $FeCl_3$/lb P for a residual soluble ortho-P of 1.5 mg P/l, and 3.1 lb $FeCl_3$/lb P for a residual of 0.5 mg P/l.

7. A method for calculating the effectiveness of dosing strong acid plus metal salt versus metal salt alone was outlined.

RECOMMENDATIONS

Further developmental work should be conducted to eliminate the discontinuity in the Ferguson & King (1977) model, particularly since the discontinuity often occurs in soluble P residual concentration regions of interest.

Laboratory experiments should be conducted to provide information on actual precipitation behavior in the discontinuity region.

Specifically, these experiments should duplicate the prototype system as much as possible. That is, they should employ simultaneous precipitation in a continuous-flow activated sludge system with precipitate recycle. The experiments should be conducted on domestic wastewater whose characteristics can be kept reasonably constant at a variety of pH, alkalinity, and initial P values.

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SECTION I

Program Flow Chart

Figure 1 gives the general program flow chart. A detailed flow chart for the computation of soluble phosphate residual is given in Figure 2.

APPENDIX II

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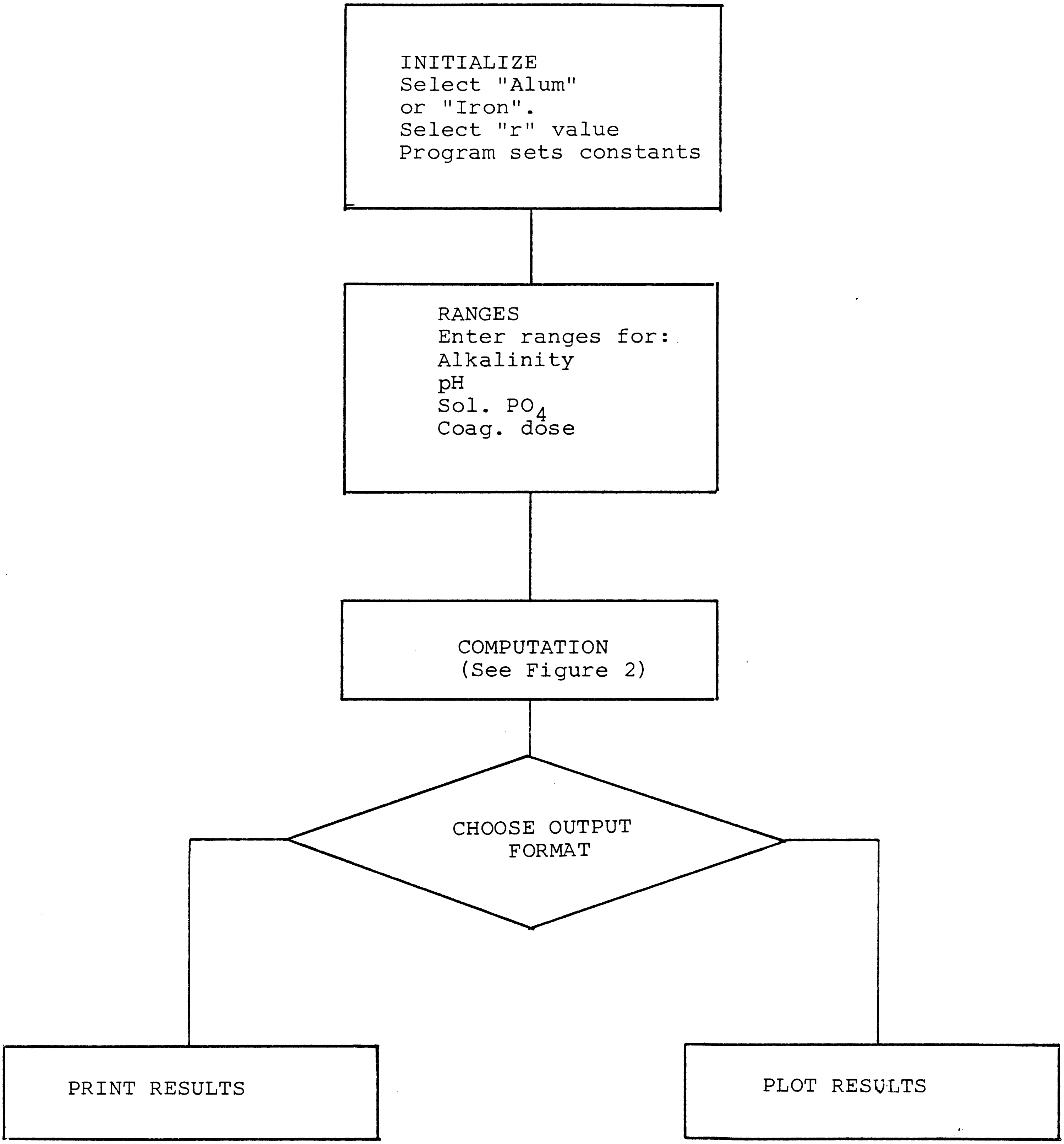

FIGURE 1 Program Flow Chart

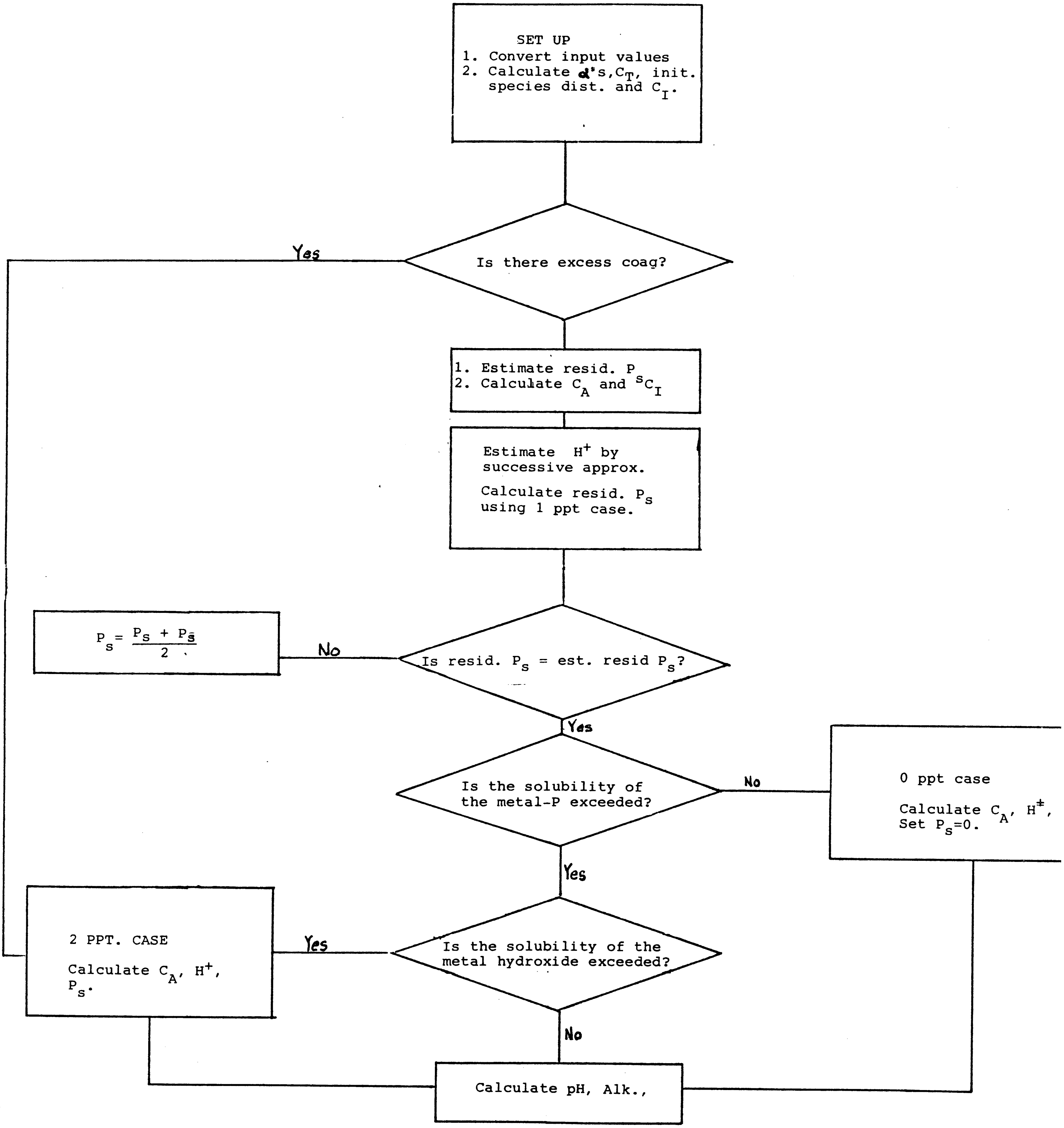

FIGURE 2 Flow Chart of Computation

SECTION II

DERIVATION OF ALGORITHM

The model is set up to estimate final soluble orthophosphate residual for given doses of alum or ferric chloride, based on the following information about the initial solution conditions:

1. Alkalinity in mg/l as $CaCO_3$
2. pH
3. Initial soluble orthophosphate concentration in mg P/l.

The first step is to convert the inputs into the units used in the calculations:

1. $$\text{Alk, eq/l} = \frac{\text{Alkalinity, mg/l as } CaCO_3}{50{,}000}$$

2. $$P_T\text{, moles/l} = \frac{\text{Soluble Phosphate, mg/l as P}}{31{,}000}$$

3. $$[H^+] = 10^{-pH}$$

INITIAL SOLUTION CONDITION

The next step is to calculate the initial solution condition from input information and equilibrium constants for phosphate and carbonate species. The equilibrium constants are given in Table 1.

For the carbonate system:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+ \qquad K_{c1}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_{c2}$$

for $C_T = 1$

$[H_2CO_3^*] = \alpha_{c0}$ (not present in significant quantities in pH range of interest)

$[HCO_3^-] = \alpha_{c1}$

$[CO_3^{2-}] = \alpha_{c2}$

$$\alpha_{c1} = \frac{1}{\frac{[H^+]}{K_{c1}} + 1 + \frac{K_{c2}}{[H^+]}}$$

$$\alpha_{c2} = \frac{\alpha_{c1} K_{c2}}{[H^+]}$$

Where:

$$C_T = \frac{\text{Alk.} - \frac{K_w}{[H^+]} - P_T\alpha_{p2} - 2P_T\alpha_{p3} + [H^+]}{\alpha_{c1} + 2\alpha_{c2}}$$

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TABLE 1

Equilibrium Relationships used in the Alum Precipitation Model

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	$K_{p2} = 10^{-7.21}$
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	$K_{p3} = 10^{-12.3}$
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	$K_{c_1} = 10^{-6.3}$
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	$K_{c2} = 10^{-10.3}$
$H_2O \rightleftharpoons H^+ + OH^-$	$K_w = 10^{-14.0}$
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$	$*K_1 = 10^{-5.0}$
$AlOH^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+$	$*K_2 = 10^{-3.7}$
$Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)^\circ_{3(aq)} + H^+$	$*K_3 = 10^{-6.5}$
$Al(OH)^\circ_{3(aq)} + H_2O \rightleftharpoons Al(OH)_4^- + H^+$	$*K_4 = 10^{-8.1}$
$Al^{3+} + H_2PO_4^- \rightleftharpoons AlH_2PO_4^{2+}$	$K = 10^{+6}$
$Al_r PO_4 (OH)_{3r-3} (s) \rightleftharpoons r\, Al^{3+} + PO_4^{3-} + (3r-3)OH^-$	$K_{so} = 10^{(-25r+1)}$
$Al(OH)_3 (s) + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$	$*K_{so} = 10^{+10.3}$

This expression can be simplified by eliminating species that are insignificant in the pH range of interest to:

$$C_T = \frac{Alk - P_T \alpha_{p2}}{\alpha_{c1}}$$

Similarly for the Phosphate system:

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad K_{p1}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_{p2}$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_{p3}$$

for $P_T = 1$

$[H_3PO_4] = \alpha_{p0}$ (not significant in pH range of interest)

$[H_2PO_4^-] = \alpha_{p1}$

$[HPO_4^{2-}] = \alpha_{p2}$

$[PO_4^{3-}] = \alpha_{p3}$

$$\alpha_{p1} = \frac{[H^+]}{K_{p2}} \alpha_{p2}$$

$$\alpha_{p2} = \frac{1}{1 + \frac{[H^+]}{K_{p2}} + \frac{[H^+]^2}{K_{p1} K_{p2}} + \frac{K_{p3}}{[H^+]}}$$

$$\alpha_{P3} = \frac{K_{P3}}{[H^+]}\alpha_{P2}$$

Initial species concentrations are then calculated from α values, initial total soluble phosphate (P_T) and the initial total carbonate (C_T: calculated from initial alkalinity).

$$[H_2PO_4^-] = P_T\,\alpha_{P1}$$

$$[HPO_4^{2-}] = P_T\,\alpha_{P2}$$

$$[PO_4^{3-}] = P_T\,\alpha_{P3}$$

$$[HCO_3^-] = C_T\,\alpha_{C1}$$

$$[CO_3^{2-}] = C_T\,\alpha_{C2}$$

$$[OH^-] = \frac{K_W}{[H^+]}$$

The concentration of cations$^{(C_I)}$ in the initial solution associated with weak base anions is calculated from the electroneutrality condition. C_I is characteristic of initial conditions and is used to calculate the final pH.

$$C_I = [HPO_4^{2-}] + 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

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ADDITION OF COAGULANT

The coagulant doses are entered into the model as either $FeCl_3$ (mg Fe/l) or Alum (mg Alum/l). These then are converted to total aluminum (AL_T) or total iron (Fe_T)

$$AL_T = \frac{\text{Alum dose, mg/l}}{300{,}000 \text{ mg/M}}$$

$$Fe_T = \frac{FeCl_3 \text{ dose, mg/l}}{56{,}000 \text{ mg/M}}$$

The equilibrium constants for the aluminum hydroxide species (Table 1) were those derived by Parks, G.A. in "Free Energies of Formation and Aqueous Solubilities of Aluminum Hydroxide and Oxide Hydroxides at 25°C." American Mineralogist, 57 1163 (1972). These are the same equilibria that were used by Ferguson and King (1977).

Ferguson and King (1977) selected the stoichiometric relationship between aluminum and phosphate in the precipitate based on a review of engineering studies of the aluminum phosphate precipitation process.

They found values were predominantly in the range of 1.4 to 1.9 and they chose 1.4 for their work. In this model the ratio (R) is a variable that can be changed by the user. The default value for R is 1.4.

Equilibrium constants for the ferric hydroxide species were taken from Stumm and Morgan, <u>Aquatic Chemistry</u>. The equilibrium constants for the iron phosphate solids and complexes (Table 2) were derived as follows using the data of Recht and Ghassemi (FWQA) Rept. 17010 EKI, "Kinetics and Mechanism of Precipitation and nature of precipitate obtained by addition of Fe (III) and Al (III) to phosphate. (Figure 7 p. 30.)

- pH of minimum dissolved phosphate = 4.
- dissolved PO_4-P concn. = 0.07 mg P/l

  $= 2.26 \times 10^{-6}$ M/l
- Stoichiometry assuming all Fe is ppted.

$$\frac{\Delta P}{\Delta Fe} = \frac{12-6.5}{12-6} = \frac{5.5}{6} = \frac{1}{1.2}$$

$\therefore (Fe^{+3})_{1.2} (PO_4^{3-}] (OH^-)_{0.6} = K_{so}$

α_{P3} (phosphoric acid) @ pH 4 $= 10^{-11.4}$

$\therefore [PO_4^{3-}] = \alpha_{P3} P = 10^{-11.4} * 10^{-5.65} = 10^{-17.05}$

Trial 1

For k_{so} of $(Fe^{3+})_{1.2} (PO_4^{3-}) (OH^-)_{0.6}$

$[Fe^{3+}]$ - from solubility of $Fe(OH)_{3(s)}$ (K_{s1})

K_{s1} (Stumm + Morgan, Aquatic Chemistry, Table 5-1)

$K_{s1} = 10^{+2.5}$ for reaction

$$Fe(OH)_{3(s)} + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$$

@ pH 4, $Fe^{3+} = 10^{+2.5} \times 10^{-4} = 10^{-9.5}$

$\therefore K_{so} - (10^{-9.5})^{1.2} (10^{-17.05}) (10^{-10})0.6 = 10^{-34.45}$

Prepare log concentration /pH diagram to fit Recht & Ghassemi results:

From K_{so} $(Fe_{1.2} PO_4 (OH^-)_{0.6(s)})$

$\log[PO_4^{3-}] + 1.2 \log[Fe^{3+}] + 0.6 \log[OH^-] = \log k_{so}$

$\log[PO_4^{3-}] + 1.2 \log[Fe^{3+}] + 0.6(-14 + pH) = -34.45$

From K_{so1} $(Fe(OH)_{3(s)})$

$$\log[Fe^{3+}] = 2.5 + 3\log[H^+] = 2.5 - 3pH$$

$$\therefore \log[PO_4^{3-}] + 1.2(2.5 - 3pH) + 0.6(-14 + pH) = -34.45$$

$$\therefore \log[PO_4^{3-}] = -29.05 + 3pH \quad — ①$$

This equation gives PO_4^{3-} in equilibrium with $Fe(OH)_{3(s)}$ and $Fe_{1.2}PO_4(OH^-)_{0.6(s)}$.

To derive equations for Iron phosphate complexes that allow production of a log concentration/pH diagram that fits the Recht & Ghassemi results, we must derive relationships for HPO_4^{2-} and $H_2PO_4^-$ and the Fe complexes of these species.

$$[PO_4^{3-}][H^+]/[HPO_4^{2-}] = 10^{-12.2} \quad (K_3, H_3PO_4)$$

$$\therefore \log[HPO_4^{2-}] = +12.2 + \log[PO_4^{3-}] - pH$$

from ① $\log[PO_4^{3-}] = -29.05 + 3pH$

$$\therefore \log[HPO_4^{2-}] = -16.85 + 2pH \quad — ②$$

$$[HPO_4^{2-}][H^+]/[H_2PO_4^-] = 10^{-7.2} \quad (K_2, H_3PO_4)$$

$\therefore \log[H_2PO_4^-] = 7.2 + \log[HPO_4^{2-}] + \log[H^+]$

substituting from ②

$\log[H_2PO_4^-] = -9.65 + pH$ — ③

For Iron phosphate complexes:

$FeHPO_4^+ \rightleftharpoons Fe^{3+} + HPO_4^{2-}$ $K = 10^{-8.3}$ (Stumm + Morgan)

$\therefore \log[FeHPO_4^+] = \log K + \log[Fe^{3+}] + \log[HPO_4^{2-}]$

and using ② :

$\log[FeHPO_4^+] = -6.05 - pH$ — ④

$\therefore \log[FeH_2PO_4^{2+}] = \log K + \log[Fe^{3+}] + \log[H_2PO_4^-]$

and using ③

$\log[FeH_2PO_4^{2+}] = -5.35 - 2pH$

These equations are plotted in Figure as a first trial to duplicate the Recht & Ghassemi solubility data. The data is not well duplicated at the region below pH 4 where solubility increases; also the pH of minimum solubility (4) is not agreed with. To obtain these

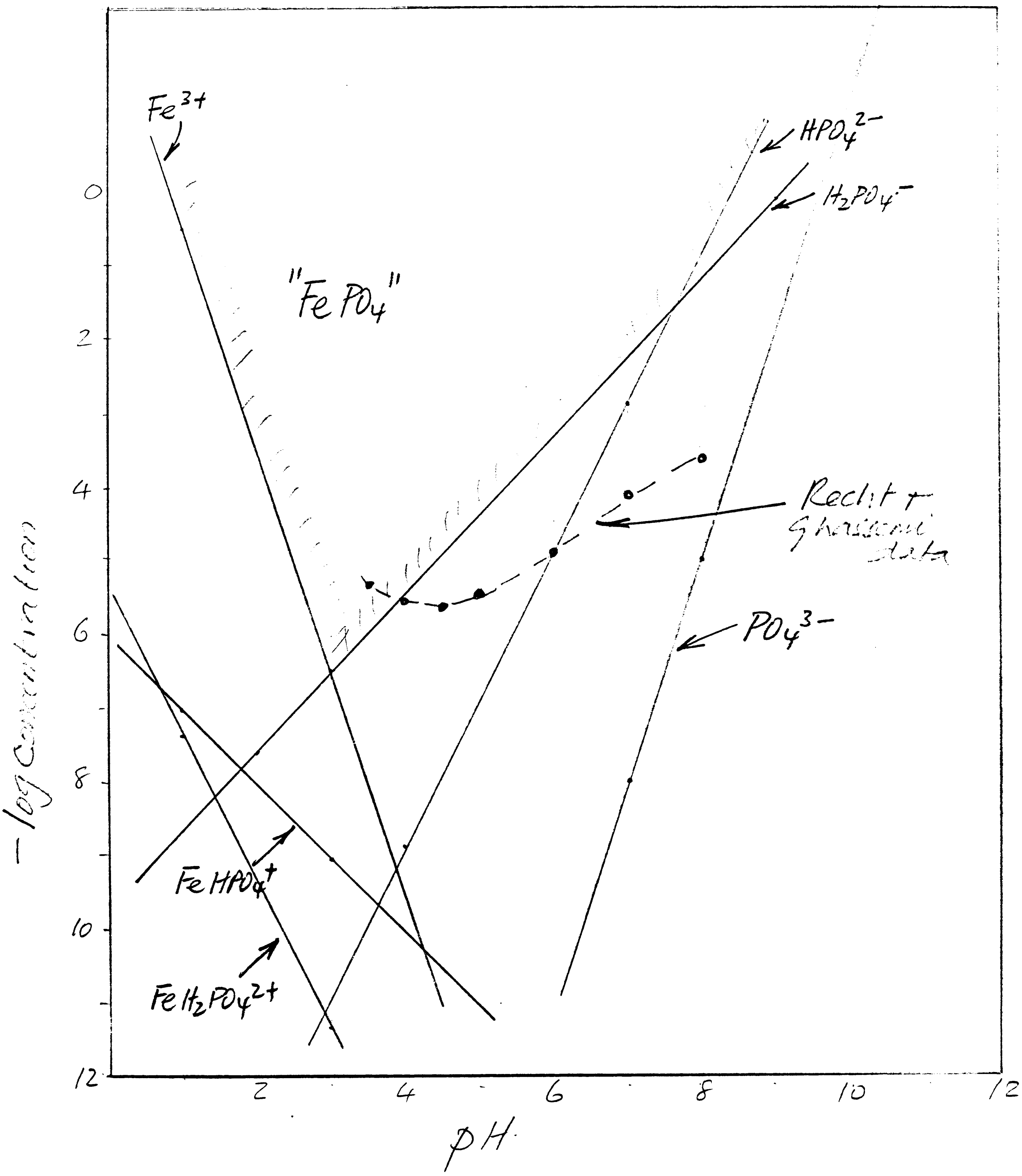

Figure First trial at duplication of Recht and Ghassemi data.

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agreements we will neglect the $FeHPO_4^+$ complex and adjust the value of the $FeH_2PO_4^{2+}$ complex. This follows.

Empirical stability constant for $FeH_2PO_4^{2+}$ is calculated from a graph adjusted to Recht & Ghassemi (Figure)

$\log[FeH_2PO_4^{2+}] = \log K + \log[Fe^{3+}] + \log[H_2PO_4^{2-}]$

@ pH 3, from diagram in Figure

$\log[FeH_2PO_4^{2+}) = -2.4$; $\log[Fe^{3+}] = -3.4$; $\log[H_2PO_4^{2-}] = -9$

$\therefore \log K = 10$

New value of $\log K_{so}$ from Figure

$\log[PO_4^{3-}] = \log K_{so} - 1.2(\log[Fe^{3+}] - 0.6\log[OH^-])$

@ pH 6, $\log[OH^-] = -8$; $\log[PO_4^{3-}] = -13.3$; $\log[Fe^{3+}] = -15.2$

$\therefore \log K_{so} = -36.3$

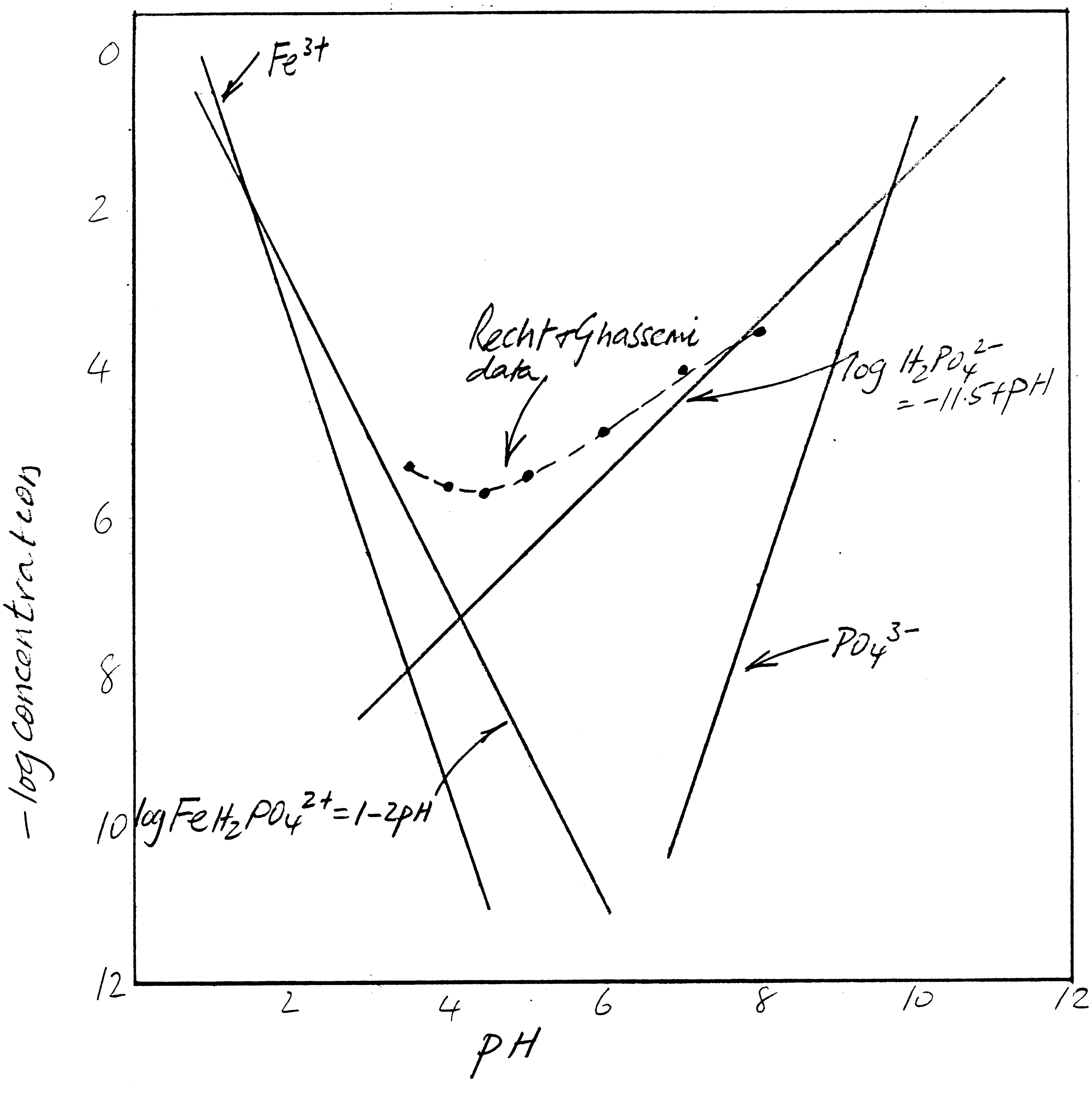


Figure Second trial at duplication of Recht & Ghassemi data

TABLE 2

EQUILIBRIUM RELATIONSHIPS USED IN THE IRON-PHOSPHATE PRECIPITATION MODEL

	log K
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	-7.2
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	-12.2
$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$	-2.2
$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$	-3.5
$Fe(OH)_2^+ + H_2O \rightleftharpoons Fe(OH)_{3(s)}^0 + H^+$	-7.3
$FeOOH_{(s)} + 3H^+ \rightleftharpoons Fe^{3+} + 2H_2O$	+2.5
$Fe_{1.2}PO_4(OH)_{0.6(s)} \rightleftharpoons 1.2\,Fe^{3+} + PO_4^{3-} + 0.6\,OH^-$	-36.3
$Fe^{3+} + H_2PO_4^- \rightleftharpoons FeH_2PO_4^{2+}$	+10

SELECTION OF PRECIPITATION ZONE

The model uses different relationships to predict final phosphate residual depending on whether the metal dose is:

1. Insufficient to precipitate any phosphate (zero ppt zone)
2. Less than or equal to the stoichiometric dose (One ppt. zone)
3. Sufficiently greater than the stoichiometric dose to precipitate metal hydroxide as well as metal phosphate (Two ppt. zone)

The critical assumption here is that the metal phosphate precipitates before the metal hydroxide.

Because the calculations to determine phosphate residual and final pH are the same for either iron or alum from this point onwards, except for the value of the constants, only the alum precipitation calculation will be presented.

As a first approximation, the model selects the two ppt region if $R(P_T + 10^{-4}) < Al_T$. If $Al_T \geq R(P_T + 10^{-4})$ it selects the zero or one ppt regions. If the model finds that there is excess alum after the phosphate residual has been estimated it will proceed to the two ppt. region calculation.

ONE PRECIPITATE REGION CALCULATION (Stoichiometric Removal)

Mass balances on phosphate and metal are solved to find the phosphate residual in this region (where only aluminum phosphate ($Al_r PO_4 (OH)_{3r-3}$ is assumed to have precipitated. These mass balances are reduced to a polynomial equation in $[H^+]$ which is solved to determine final $[H^+]$ concentration. The value for P_S (soluble phosphate residual) is then calculated for this $[H^+]$.

Since final $[H^+]$ is dependent on P_S, it is necessary to solve the equations simultaneously to arrive at the correct final pH and P_S.

$[H^+]$ Calculation for the 1 PPT Region

The final $[H^+]$ is a function of the original electroneutrality condition (C_I), the acidity added by the alum (C_A), $[OH]$

and the final species distribution of carbonate and phosphate species

The protons released (C_A) by the reactions involved in aluminum phosphate precipitation follow a stoichiometry that depends on the initial concentrations of HPO_4^{2-} and $H_2PO_4^-$:

$$r\,Al^{3+} + HPO_4^{2-} + (3r-3)\,H_2O \rightleftharpoons Al_r\,PO_4\,(OH)_{3r-3\,(s)} + (3r-2)\,H^+$$

$$[H^+]\,\text{released} / [Al^{+3}] = \frac{3r-2}{r}$$

$$r\,Al^{3+} + H_2PO_4^- + (3r-3)\,H_2O \rightleftharpoons Al_r\,PO_4\,(OH)_{3r-3(s)} + (3r-1)\,H^+$$

$$[H^+]\,\text{released} / [Al^{+3}] = \frac{3r-1}{r}$$

In the 1 PPT region the amount of phosphate precipitated is a function of the alum dose and not the initial total phosphate

$$\therefore C_A = \frac{(3r-2)(\alpha_{p20}) + (3r-1)\,\alpha_{p10}}{r}\,AL_T$$

The final electroneutrality condition is:

$$C_I - C_A = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [HPO_4^{2-}] - [H^+] \quad ①$$

where:

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$[CO_3^{2-}] = C_T \alpha_{C2} = C_T \alpha_{C1} \frac{K_{C2}}{[H^+]}$$

$$[HCO_3^-] = C_T \alpha_{C1} = C_T \left[\frac{1}{\frac{[H^+]}{K_{C1}} + 1 + \frac{K_{C2}}{[H^+]}} \right]$$

$$[HPO_4^-] = P_S \alpha_{P2} = P_S \left[\frac{1}{1 + \frac{[H^+]}{K_{P2}} + \frac{[H^+]^2}{K_{P1}K_{P2}} + \frac{K_{P3}}{[H^+]}} \right]$$

The program solves this equation (①) by defining a function:

$$f([H^+]) = C_A + [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [HPO_4^{2-}] - [H^+] - C_I$$

It then solves for $f([H^+]) = 0$ by successive approximations recalculating the species concentrations each time through the loop. The $[H^+]$ is then used to calculate P_S as shown below

P_s Calculation for the 1 PPT Region

P_s for the 1 PPT region is determined from the mass balances:

$$AL_T = r[Al_r PO_4(OH)_{3r-3(s)}] + [Al^{+3}] + [AlOH^{2+}] + [Al(OH)_2^{+}] + [Al(OH)_3^{\circ}] + [Al(OH)_4^{-}] + [AlH_2PO_4^{2+}]$$

$$P_T = [Al_r PO_4(OH)_{3r-3(s)}] + [H_2PO_4^{-}] + [HPO_4^{2-}] + [AlH_2PO_4^{2+}]$$

$$P_T - \frac{AL_T}{r} = -\frac{1}{r}\left([Al^{+3}] + [AlOH^{2+}] + [Al(OH)_2^{+}] + [Al(OH)_3^{\circ}] + [Al(OH)_4^{-}]\right) + [H_2PO_4^{-}] + [HPO_4^{2-}] + \frac{(r-1)}{r}[AlH_2PO_4^{2+}] \quad ②$$

Equilibrium constant relationships among the soluble species are used to reduce ② to a polynomial equation with $[PO_4^{3-}]$ as the single variable:

1. $[Al^{3+}]$

$$Al_r PO_4(OH)_{3r-3(s)} \rightleftharpoons rAl^{3+} + PO_4^{3-} + (3r-3)\,OH^-$$

$$[Al^{3+}]^r[PO_4^{3-}][OH^-]^{3r-3} = K_{so}$$

$$[Al^{3+}] = \frac{K_{so}^{1/r}}{[PO_4^{3-}]^{1/r}\left(\frac{K_w}{[H^+]}\right)^{\frac{3r-3}{r}}}$$

2. $[AlOH^{2+}]$

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \qquad *K_1$$

$$\frac{[AlOH^{2+}][H^+]}{[Al^{+3}]} = *K_1$$

$$[AlOH^{2+}] = \frac{*K_1 [Al^{3+}]}{[H^+]}$$

3. $[Al(OH_2^+]$

$$AlOH^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+ \qquad *K_1$$

$$[Al(OH)_2^+] = \frac{*K_2}{[H^+]}[AlOH^{2+}] = \frac{*K_1 *K_2}{[H^+]^2}[Al^{+3}]$$

4. $[Al(OH)_3^\circ]$

$$Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)_3^0 + H^+ \qquad *K_3$$

$$[Al(OH)_3^\circ] = \frac{*K_3}{[H^+]}[Al(OH)_2^+] = \frac{*K_3 *K_2 *K_1}{[H^+]^3}[Al^{3+}]$$

5. $[Al(OH)_4^-]$

$$Al(OH)_3^0 + H_2O \rightleftharpoons Al(OH)_4^- + H^+ \qquad *K_4$$

$$[Al(OH)_4^-] = \frac{*K_4}{[H^+]}[Al(OH)_3^\circ] = \frac{*K_4 *K_3 *K_2 *K_1 [Al^{+3}]}{[H^+]^4}$$

6. $[HPO_4^{2-}]$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_{p3}$$

$$[HPO_4^{2-}] = \frac{[PO_4^{3-}][H^+]}{K_{p3}}$$

7. $[H_2PO_4^-]$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_{p2}$$

$$[H_2PO_4^-] = \frac{[HPO_4^{2-}][H^+]}{K_{p2}} = \frac{[PO_4^{3-}][H^+]^2}{K_{p2}K_{p3}}$$

8. $[AlH_2PO_4^{2+}]$

$$Al^{3+} + H_2PO_4^- \rightleftharpoons AlH_2PO_4^{2+} \qquad K$$

$$\frac{[AlH_2PO_4^{2+}]}{[Al^{3+}][H_2PO_4^-]} = K$$

$$[AlH_2PO_4^{2+}] = K[Al^{3+}][H_2PO_4^-]$$

$$[AlH_2PO_4^{2+}] = K\left(\frac{K_{so}^{1/r}\,[H^+]^{\frac{3r-3}{r}}}{[PO_4^{3-}]^{1/r}\,K_w^{\frac{3r-3}{r}}}\right)\left(\frac{[PO_4^{3-}][H^+]^2}{K_{p2}K_{p3}}\right)$$

Substituting back into equation ②:

$$P_T - \frac{AL_T}{r} = \frac{-1}{r}\left(\frac{K_{so}^{1/r}\,[H^+]^{\frac{3r-3}{r}}}{[PO_4^{3-}]^{1/r}\,K_w^{\frac{3r-3}{r}}}\right)\left(1 + \frac{{}^*K_1}{[H^+]} + \frac{{}^*K_1{}^*K_2}{[H^+]^2} + \frac{{}^*K_3{}^*K_2{}^*K_1}{[H^+]^3} + \frac{{}^*K_4{}^*K_3{}^*K_2{}^*K_1}{[H^+]^4}\right.$$

$$\left. + [PO_4^{3-}]\left(\frac{[H^+]}{K_{p3}} + \frac{[H^+]^2}{K_{p2}K_{p3}}\right) + [PO_4^{-3}]^{\frac{r-1}{r}}\left(\frac{K\,K_{so}^{1/r}\,[H^+]^{\frac{5r-3}{r}}}{K_w^{\frac{3r-3}{r}}\,K_{p2}K_{p3}}\right)\right)$$

This relationship can be solved for $[PO_4^{3-}]$ by successive approximations. P_s is then calculated from the relationship:

$$P_s = [H_2PO_4^-] + [HPO_4^{2-}] + [AlH_2PO_4^{2+}]$$

$$P_s = [PO_4^{3-}]\left(\frac{[H^+]}{K_{p3}} + \frac{[H^+]^2}{K_{p2}K_{p3}}\right) + \frac{K\,K_{so}^{1/r}\,[H^+]^{\frac{5r-3}{r}}}{K_{p2}\,K_{p3}\,K_w^{\frac{3r-3}{r}}}\,[PO_4^{3-}]^{\frac{r-1}{r}}$$

This value for P_s is then compared with the value of P_s used in the calculation of $[H^+]$ if they differ by more than 0.1 the calculation of $[H^+]$ and P_s is repeated using an average of the old and new values for . P_s.

The program then rechecks to determine whether the correct region was chosen by checking for 0 PPT or 2 PPT.

There is 0 PPT if the $[Al_r PO_4(OH)_{3r-3(s)}]$ concn. does not exceed the solubility product:

$$Al_r PO_4(OH)_{3r-3(s)} \rightleftharpoons r Al^{3+} + PO_4^{3-} + (3r-3) OH^- \qquad K_{so}$$

if $K_{so} < [Al^{3+}]^r [PO_4^{3-}] [OH^-]^{3r-3}$ there is 0 PPT

The 2 PPT region is pertinent if there is sufficient $[Al^{3+}]$ remaining after aluminum phosphate precipitates to precipitate aluminum hydroxide.

1. $Al(OH)_{3(s)} + 3H^+ \rightleftharpoons Al^{+3} + H_2O \qquad *K_{so}$

$$[Al^{3+}]_{limit} = K_{so}[H^+]^3$$

2. $Al_r PO_4(OH)_{3r-3(s)} \rightleftharpoons r Al^{+3} + PO_4^{3-} + (3r-3) OH^- \qquad K_{so}$

$$[Al^{3+}]_{Available} = \frac{K_{so}^{1/r}}{[PO_4^{3-}]^{1/r}\left[\frac{K_w}{[H^+]}\right]^{\frac{3r-3}{r}}}$$

3. If $\frac{[Al^{3+}]_{avail.}}{[Al^{3+}]_{limit}} > 1.2$ and $Al_T - RP_T > 0$ then 2 ppts.

0 PPT REGION

In cases where there are wastewaters with a high initial alkalinity and pH low alum doses might not precipitate any phosphate. When this happens the final pH and alkalinity is a function of the initial solution conditions and the final species distribution of the phosphate, carbonate and aluminum systems.

$$F([H^+]) = C_I + [H^+] - [OH^-] + C_T(\alpha_{C1} + 2\alpha_{C2}) + P_T(\alpha_{P2} + 2\alpha_{P3})$$
$$+ Al_T(\alpha_{a0} + \alpha_{a1} + \alpha_{a2} + \alpha_{a3})$$

2 PPT REGION

In the 2 ppt region two solubility relationships control:

$$Al(OH)_{3(s)} + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O \qquad {}^*K_{so}$$

$$Al_r PO_4(OH)_{3r-3(s)} \rightleftharpoons rAl^{3+} + PO_4^{3-} + (3r-3)OH^- \qquad K_{so}$$

The aluminum hydroxide solubility product determines the concentration of soluble aluminum that can exist.

This apparently introduces a discontinuity into the model since in the 1ppt region the $Al_rPO_4(OH)_{3r-3}$ precipitation was assumed to be the controlling reaction. At pH values above ___ virtually all the aluminum is shown to react to form aluminum hydroxide so little or no phosphate removal is shown.

The acidity added to the solution (C_A) is determined by the $[H^+]$ added by the reactions of alum to precipitate $Al_rPO_4(OH)_{3r-3(s)}$ or $Al(OH)_{3(s)}$ and depends on the initial proportions of HPO_4^{2-} and $H_2PO_4^-$:

$$rAl^{3+} + HPO_4^{2-} + (3r-3)H_2O \rightleftharpoons Al_rPO_4(OH)_{3r-3(s)} + (3r-2)H^+$$

$$\frac{[H^+]\text{released}}{[Al^{3+}]} = \frac{3r-2}{r}$$

$$rAl^{3+} + H_2PO_4^- + (3r-3)H_2O \rightleftharpoons Al_rPO_4(OH)_{3r-3(s)} + (3r-1)H^+$$

$$\frac{[H^+]\text{released}}{[Al^{3+}]} = \frac{3r-1}{r}$$

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)_{3(s)} + 3H^+$$

$$\frac{[H^+]\text{released}}{[Al^{3+}]} = 3$$

$$[Al(OH)_{3(s)}] = AL_T - RP_T$$

$$C_A = 3\left[AL_T - RP_T\right] + P_T\left[(3r-2)\alpha_{p2} + (3r-1)\alpha_{p1}\right]$$

(soluble aluminum species can be neglected)

$[H^+]$ Calculation for 2 PPT Region

The final $[H^+]$ then is calculated from the electroneutrality condition:

$$F([H^+]) = -C_I - [H^+] + C_A + [HCO_3^-] + 2[CO_3^{2-}]$$

(soluble phosphate and aluminum species are not present in significant quantities)

putting $[HCO_3^-]$ and $[CO_3^{2-}]$ in terms of constants and $[H^+]$ and total carbonate concn.:

$$F([H^+]) = -C_I - [H^+] + C_A + C_T\left(\frac{1}{\frac{[H^+]}{K_{c1}} + 1 + \frac{K_{c2}}{H^+}}\right)\left(1 + \frac{2K_{c2}}{[H^+]}\right)$$

P_3 Calculation for 2 PPT Region

The final $[PO_4^{3-}]$ concentration is calculated from the precipitation reactions for $Al(OH)_{3(s)}$ and $Al_rPO_4(OH)_{3r-3(s)}$.

$$Al_rPO_4(OH)_{3r-3(s)} \rightleftharpoons rAl^{3+} + PO_4^{3-} + (3r-3)OH^- \qquad K_{so}$$

$$[PO_4^{3-}] = \frac{K_{so}}{[Al^{3+}]^r[OH^-]^{3r-3}}$$

$$Al(OH)_{3(s)} + 3H^+ \rightleftharpoons Al^{3+} + H_2O \qquad {*K_{so}}$$

$$\frac{[Al^{3+}]}{[H^+]^3} = {*K_{so}}$$

$$[Al^{3+}] = {*K_{so}}[H^+]^3$$

$$[PO_4^{3-}] = \frac{K_{so}}{({*K_{so}}[H^+]^3)^r \dfrac{K_w^{3r-3}}{[H^+]^{3r-3}}}$$

$$= \frac{K_{so}}{{*K_{so}}^r[H^+]^3K_w^{3r-3}}$$

2 ppt
$[PO_4^{3-}] = f\,[H^+]$ only

The final P_s concentration is a sum of the soluble species:

$$P_s = [HPO_4^{2-}] + [H_2PO_4^-] + [AlH_2PO_4^{2+}]$$

$[HPO_4^{2-}]$ and $[H_2PO_4^-]$ can be expressed in terms of constants and $[H^+]$ as was shown in the calculations for the one ppt region. AlH_2PO_4 can also be expressed in terms of constants and $[H^+]$ as shown below:

$$Al^{3+} + H_2PO_4^- \rightleftharpoons AlH_2PO_4^{2+} \qquad K$$

$$\frac{[AlH_2PO_4^{2+}]}{[Al^{3+}][H_2PO_4^-]} = K$$

$$[AlH_2PO_4^{2+}] = \frac{K(*K_{s0})[H^+]^5[PO_4^{3-}]}{K_{p2}K_{p3}}$$

Substituting back:

$$P_S = [PO_4^{3-}]\left(\frac{[H^+]}{K_{p3}} + \frac{[H^+]^2}{K_{p2}K_{p3}} + \frac{K(*K_{s0})[H^+]^5}{K_{p2}K_{p3}}\right)$$

OUTPUTS

In all cases after a final P_S and $[H^+]$ are determined, the program calculates the final pH, alkalinity, soluble phosphate residual (in mg/l as P). It then prints or plots the results.

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [H_2PO_4] + 2[HPO_4^{2-}] + [OH^-] - [H^+]$$

$$pH = -\log[H^+]$$

```
----------=====******   1 ******=====----------
\ VARIABLE TRACE (FIG DEPENDENT)
DECIMAL
HERE FIRST OVER - ERASE
CREATE TASK
VARIABLE DEPTH-TRACE
VARIABLE VAR-TRACE

: F! ( FP ADDR --- )
  DEPTH-TRACE @
  IF CR ." (" DEPTH 4 -
     2 .R ." ) "
  THEN VAR-TRACE @
  IF ( TRACING )
     DEPTH-TRACE @ NOT IF CR THEN
    ( ONLY ONE CR )
  DUP NFA ( FIG ) ID. #OUT @
  20 MOD 20 SWAP - SPACES ." = "
  >R FDUP F. R> THEN F! ;

   -->
```

REDO THE DEFINITION OF FVARIABLE
SO THAT, VAR-TRACE IS TURNED ON.

ITS NEW CONTENTS WILL BE PRINTED
WHENEVER SOMETHING IS STORED THERE
WITH F!

GREAT TRACING ROUTINE.

IF DEPTH-TRACE IS ON, THE STACK DEPTH
(OF AFTER THE STORE) IS PRINTED.

```
----------=====******   2 ******=====----------
\ REDO FOR FLOATING TRACE

VARIABLE MATH-TRACE

: REDO
  >IN @ ' SWAP >IN ! ( ADR OF PREV )
  CREATE , ( COMPILE OLD DEF )
  DOES> @ MATH-TRACE @ DUP >R
    IF >R CR ." (" DEPTH 2 .R ." ) "
      FOVER F.
  R@ 2+ NFA ID. ( FIG-FORTH )
  FDUP F. R>
    THEN EXECUTE
    R>
    IF FDUP ."     =" F.
    THEN ;

REDO F* REDO F/ REDO F+ REDO F-  REDO F↑

MATH-TRACE OFF
-->
```

"REDO" MAKES A NEW DEFINITION OF THE
NEXT INLINE WORD, A FLOATING POINT
OPERATION, SO THAT IT WILL BE TRACED
IF THE VARIABLE MATH-TRACE IS
TURNED ON.

```
------======******  3 ******======------
\ DEFERRED WORD WORDS
: CRASH
  TRUE ABORT" ***CRASH*** HA HA HA" ;

: DEFER
  CREATE [']  CRASH ,
  DOES> @ EXECUTE ;

: (IS) R> DUP 2+ >R @ >BODY ! ;


: IS
  STATE @ IF COMPILE (IS)
  ELSE '  >BODY ! THEN ; IMMEDIATE


-->
```

THESE ARE THE STANDARD WORDS FOR MAKING DEFERRED WORDS. THEY ARE COMPILED ON THE OLD SCI-4TH SINCE IT DOESN'T HAVE THEM....

```
------======******  4 ******======------
\ FIX AND UNFIX "<" AND ">"

: FIX ( SCR# --- )
  BLOCK 1024 OVER + SWAP DO
   I C@ ASCII < =

   IF 123 ( LBRACE ) I C!
   THEN I C@ ASCII > =
   IF 125 ( RBRACE ) I C!
   THEN
  LOOP ;

: UNFIX ( SCR# --- )
  BLOCK 1024 OVER + SWAP DO
   I C@ 123 =

   IF ASCII < I C!
   THEN I C@ 125 =
   IF ASCII > I C!
   THEN
  LOOP ;


-->
```

THIS ROUTINE FIXES A SCREEN BY CONVERTING ALL < TO A LEFT BRACKET AND ALL > TO RIGHT BRACKET.

WATCH OUT--- THE OLD SCI4TH CONVERTS THESE MARKS TO "UPPERCASE". A [AND] . THEREFORE, YOU HAVE IN EFFECT REDEFINED] AND [. SO DO NOT TRY TO GO IN AND OUT OF COMPILING MODE WITH THE [AND]! YOU CAN'T. SCI4TH SHOULD NOT EVEN BE CONVERTING THESE CHARACTERS.

THEY ARE NOT LOWERCASE!

```
----------========******   5 ******========------
\ NESTING WORDS FOR FLOATING PT.

: {  1  CSP    +! ; IMMEDIATE
: }  -1 CSP    +! ; IMMEDIATE


( SINCE COLON SETS CSP, WE INC/DEC
  THAT WHEN < AND > ARE FOUND.  IF THE
  EXPRESSION IS IMBALANCED, THERE WILL
  BE A CONTROL STRUCTURE ERROR. )

-->
```

THESE WORDS, { AND } HAVE NO REAL SIGNIFIGANCE, THEY ARE JUST USED AS AN AID FOR COMPILING. THEY ARE PLACED AROUND A SUB-EXPRESSION. OPTIONALLY, BUT EACH { MUST BE BALANCED BY A }. THIS WAY, IT WILL BE EASIER TO READ THE LISTING, AND BADLY CODED FORMULAS WILL BE EASY TO SPOT.
THEY WORK BY INCREMENTING AND DECREMENTING CSP. : AND ; REQIRE CSP TO BE THE SAME FROM THE START TO THE END OF THE DEFINITION, SO THERE WILL BE AN ERROR IF THE NUMBER OF BRACES IS UNBALANCED, HOPEFULLY POINTING OUT A GOOF IN THE PROGRAMMING.
THE WORDS { AND } ARE NOT COMPILED INTO THE DICTIONARY AT ALL. THEY ARE EXECUTED IMMEDIATELY.

NOTE THAT THE APPLE SCREEN DOES NOT DISPLAY/INPUT THE BRACE CHARACTERS.

```
----------========******   6 ******========------
\ INPUT VARIABLES   DOSE-NAME

FVARIABLE ALKALINITY(MG/L)
FVARIABLE PHOSPHATE.CONC(MG/L)

FVARIABLE PH.INPUT
FVARIABLE ALUM.DOSE(MG/L)
FVARIABLE R 1.4 R F!
     ( FOR STARTING UP AS ALUM )

DEFER DOSE-NAME

: "ALUM" ." ALUM " ;
: "IRON" ." IRON " ;

' "ALUM" IS DOSE-NAME

( INITIALIZE TO BE ALUM )


-->
```

THESE ARE THE INPUT VALUES.
THE ALKALINITY, PHOSPHATE CONCENTRATION, pH AND ALUM/or Iron DOSE ARE THEN CONVERTED FROM THESE VALUES TO A MORE USEABLE FORM-- THAT IS, IN UNITS OF MOLES/L OR EQ/L.

R STAYS THE SAME THROUGHOUT THE PROGRAM

```
-----------======****** 7 ******======------
\ CONSTANTS                             CONSTANTS
                                        K        _2.1       K         -7.21
10.0 -2.14  F↑      FCONSTANT KP1        P1   = 10           P2   = 10
10.0 -7.21  F↑      FCONSTANT KP2
10.0 -12.35 F↑      FCONSTANT KP3       K        _12.3      K         -14
                                         P3   = 10           W    = 10
1.0E-14             FCONSTANT KW
10.0 -6.35  F↑      FCONSTANT KC1       K        _6.3       K         -10.3
10.0 -10.3  F↑      FCONSTANT KC2        C1   = 10           C2   = 10

1.0E+6              FCONSTANT K         K        _34                   6
10.0 10.3   F↑      FCONSTANT *KSO       SO   = 10          K     = 10
1.0E-5              FCONSTANT *K1
10.0 -3.7   F↑      FCONSTANT *K2       *K        10.3      ( SET UP FOR ALUM()
10.0 -6.5   F↑      FCONSTANT *K3         SO = 10
10.0 -8.1   F↑      FCONSTANT *K4
                                       *K      -5          *K        -3.7
300000.0  FCONSTANT ALT.SCALAR           1    = 10           2    = 10
-->
( WE USE ACTUAL EXPONENTIATION DUE     *K      -6.5       -*K        -8.1
TO TRUNCATION OF POWERS                  3    = 10           4    = 10
WHEN WE USE "E" NOTATION )
                                        ( SOMETIMES PRINTER DOESN'T SHOW -'S )

-----------======****** 8 ******======------
\ ALK, PH, ALT, ALPHA VARIABLES.
                                          ALK IS THE ALKALINITY IN EG/L
FVARIABLE ALK                             PT IS P      IN MOLES/L
FVARIABLE PH                                     T
FVARIABLE ALT
                                          H+  IS INITIALLY            PH
FVARIABLE ALPHA.P1  FVARIABLE ALPHA.P10          CALCULATED TO BE 10
FVARIABLE ALPHA.P2  FVARIABLE ALPHA.P20
FVARIABLE ALPHA.P3  FVARIABLE ALPHA.P30   ALT IS AL  , ALUM DOSE IN MOLES/L
FVARIABLE ALPHA.C1  FVARIABLE ALPHA.C10            T
FVARIABLE ALPHA.C2  FVARIABLE ALPHA.C20            .

FVARIABLE ALPHA.A0                      IN THE CASE OF THE FERRIC CHLORIDE MODEL

FVARIABLE ALPHA.A1                       WE STILL USE THE WORDS THAT SIGNIFY
FVARIABLE ALPHA.A2  ( ALUMINUM ALPHAS )  ALUM INPUT.  REALLY ONLY THE CONSTANTS
FVARIABLE ALPHA.A3                       AND THE OUTPUT IS CHANGED FOR IRON.
FVARIABLE ALPHA.A4                      SINCE THE MODEL ORIGINALLY RUNS AS
                                         ALUM, WE GIVE EVERYTHING ALUM NAMES...
FVARIABLE DELTA.P
FVARIABLE DELTA.AL                      THE ALPHA VALUES ENDING IN 0
FVARIABLE SLUDGE                        CONTAIN THE ORIGINALLY CALCULATED
-->                                     VALUES.  THEY ARE SET BY THE WORD
                                        "BACKUP"
```

```
----------======****** 9 ******======------
\ SPECIES AND OTHER VARIABLES                --> THESE ARE DATA CELLS WHICH ARE CAL-
FVARIABLE CT                                 CULATED IN "CALC-SPECIES-DISTRIB"
FVARIABLE CA
                                             FIRST, C  IS CALCULATED, THEN....
FVARIABLE CO3--       FVARIABLE CO3--0               T     ---
FVARIABLE HCO3-       FVARIABLE HCO3-0       CO3--  =  CO         HCO3-  =  HCO
FVARIABLE PO4---      FVARIABLE PO4---0                  3                    3
FVARIABLE HPO4--      FVARIABLE HPO4--0                    ---
FVARIABLE H2PO4-      FVARIABLE H2PO4-0      PO4--- = PO          OH-    = OH
FVARIABLE OH-         FVARIABLE OH-0                    4
                                                            --
FVARIABLE H+          FVARIABLE H+0          HPO4-- = HPO         H2PO4- = H PO
FVARIABLE PS          FVARIABLE PS0                     4                 2  4
FVARIABLE PS.TRIAL
FVARIABLE (HCO3-)                            (HCO3-) AND (PO4---), IN PARENTHESES.
FVARIABLE (PO4---)                           ARE NOT TO BE CONFUSED WITH THE SPECIES
FVARIABLE AL+3                               DISTRIBUTION.
FVARIABLE AL+3.LIMIT                         AL+3   AND AL+3.LIMIT ARE USED IN THE

                                             SOLUBILITY-EXCEEDED ROUTINE.
FVARIABLE CI                                 PS0 IS THE INITIAL PS, SAVED WITH
                                             THE FIRST CALCULATION.
FVARIABLE PT
-->                                          PT IS TOTAL PHOSPHATE.

----------======****** 10 ******======------
\ KSO

: KSO.ALUM                                   SINCE KSO WAS ORIGINALLY DESIGNED TO
  10.0  -25.0 R F@ F* F1+   F↑  ;            BE A CONSTANT, WE WANT KSO TO RETURN
: KSO.IRON                                   A VALUE ON THE STACK.
  10.0  15.0 R F@ F* 54.6 F+ 2.0 F/
   FNEGATE F↑ ;                              SINCE WE CHANGED KSO TO BE A FUNCTION
                                             OF R, IT CAN NO LONGER BE A CONSTANT.
( STILL ACTS AS A CONSTANT )
                                             HOWEVER, TO MAINTAIN INTEGRITY. WE
                                             DO NOT MAKE KSO A VARIABLE BECAUSE SO
DEFER KSO                                    MUCH OF THE PROGRAM ALREADY EXISTS
                                             WITH KSO USED AS A CONSTANT.
' KSO.ALUM IS KSO ( START UP AS ALUM )
                                             THUS, WE HAVE IT RETURN THE VALUE ON
                                             THE STACK.

                                             A PROBLEM IS THAT THIS VALUE IS COMPUTED

                                              EVERY TIME IT'S CALLED, WHICH IS SOME-
                                              WHAT INEFFICIENT.
-->
```

```
---------------======****** 11 *****======------
\ SOLVE-TILL-CROSS
DEFER F(X)          DEFER ROOT
FVARIABLE OLD.F(X)  FVARIABLE OLD.ROOT
FVARIABLE MULT      FVARIABLE SOLUTION

: SOLVE-TILL-CROSS ( -- )
  BEGIN
    SOLUTION F@

    OLD.F(X) F!
    ROOT F@
    FDUP
    OLD.ROOT F!
    MULT F@


    F*
     ROOT  F!
    F(X)
    OLD.F(X) F@
    F*
    F0> NOT
 UNTIL ;
-->
```

MULT HOLDS THE AMOUNT TO MULTIPLY BY EACH PASS THROUGH. WE START OUT MULTIPLYING BY 10 EACH TIME TILL WE CROSS THE ROOT. THEN WE DIVIDE BY THE SQUARE ROOT OF 10 TILL WE CROSS. THEN WE MULTIPLY BY THE SQUARE ROOT OF THE SQUARE ROOT OF 10 UNTIL WE CROSS.

AND SO ON, UNTIL WE GET A CLOSE ENOUGH ANSWER.

F(X) AND ROOT ARE DEFERRED SO DIFFERENT EQUATIONS/ANSWERS CAN USE THIS EQUATION-SOLVING METHOD.

OLD.F(X) AND OLD.ROOT HOLD THE PREVIOUS X AND F(X) VALUES.

SOLVE-TILL-CROSS STARTS TRYING OUT THE ROOTS, MULTIPLYING BY "MULT" EACH TIME. UNTIL IT HAS GONE TOO FAR AND CROSSES THE X-AXIS.

```
---------------======****** 12 *****========------
\ GET-ROOT
: GET-ROOT ( --- ROOT )
  1.0E-9  ROOT F!
   F(X) OLD.F(X) F!
  10.0 FDUP MULT F!
  ROOT F@ F* ROOT F!

  F(X) FDUP OLD.F(X) F@ F* F0<
  IF   FDROP MULT F@ -0.5 F↑
    ( CROSSED AXIS ALREADY, FIX NOW )
  ELSE FDUP OLD.F(X) F@ F- F* F0>
    IF   MULT F@ -1.0 F↑
    ELSE MULT F@
    THEN ( MULT ON STACK )
  THEN
  5 0 DO ( # OF TIMES TO ITERATE )
    FDUP MULT F!
    SOLVE-TILL-CROSS -0.5 F↑
  LOOP  FDROP
  ROOT F@ OLD.ROOT F@ F+ 2.0 F/ ;
  ( TAKE AVERAGE OF LAST 2 ROOTS )
-->
```

GET-ROOT STARTS WITH A SEED OF 1E-9. IT INITIALIZES OLD.F(X) AND MULT. THEN, IT TRYS F(NEW X) AND CHECKS TO SEE IF IT HAS ALREADY CROSSED THE X AXIS. IF SO, IT GETS THE SQUARE-ROOT RECIPROCAL TO START TESTING IN THE OTHER DIRECTION AND WITH SMALLER INCREMENTS. OTHERWISE, IT CHECKS IF THE Y VALUE IS FARTHER AWAY FROM THE X AXIS THAN THE PREVIOUS Y VALUE. IF SO, IT REVERSES THE DIRECTION OF THE TESTING BY SETTING MULT TO ITS RECIPROCAL.

THEN, IN A LOOP, IT APPLIES THE TRIAL ROOTS TO THE FORMULA UNTIL THE X-AXIS IS CROSSED. THEN IT ALTERS MULT TO REVERSE DIRECTION WITH SMALLER INCREMENTS, AND REPEATS. WHEN THIS IS DONE, THE ROOT IS DETERMINED BY TAKING THE AVERAGE OF THE LATEST ROOT AND THE PREVIOUS ROOT.

```
-----------======****** 13 **********======------
-->
```

```
------======****** 14 *********======------
\ CONVERT-INPUTS                                -->
: INIT:ALK ( --- )                              THESE ARE THE AOS/ENGLISH REPRESENTA-
  { ALKALINITY(MG/L) F@ 50000.0 F/ }            TIONS OF THE CALCULATIONS. (":=", AS
  ALK F! ;                                      IN PASCAL, MEANS "GETS")
: INIT:PH  ( --- )
  PH.INPUT F@ PH F! ;                                                    ALK.MG/L AS CACO3

: INIT:PT ( --- )                               ALKALINITY, EQ/L    := ----------------

  { PHOSPHATE.CONC(MG/L) F@ 31000.0 F/ }                                    50.000
  PT F! ;
                                                                PHOSPHATE IN MG/L AS P
: INIT:H+  ( --- )                              P   MOLES/L  :=  ---------------------
  { 10.0 { PH F@ FNEGATE } F↑ }                  T                          31.000
  H+ F! ;
                                                                -PH
: INIT:ALT ( --- )                              H+   :=    10
  ALUM.DOSE(MG/L) F@ ALT.SCALAR F/
  ALT F! ;                                                ALUM (FECL) DOSE IN MG/L
                                                AL   := ----------------
: CONVERT-INPUTS INIT:ALK INIT:PT                 T          MOLES/MG
  INIT:PH INIT:H+ INIT:ALT ;
-->                                             AL  IS THE ALUM DOSE OR FECL DOSE IN
                                                  T    MILLIGRAMS/LITER. MOLES/MG IS
                                                   300000 (ALUM) OR 56000 (IRON).
```

```
------=======****** 17 ******=======------
\ CALC:A.C1 CALC:A.C2  CALC-ALPHAS      -->

: CALC:A.C1 ( --- )                                             1
  { 1.0                                 ALPHA  := -----------------------------
    { { H+ F@ KC1 F/         }               C1                    K
      { 1.0                  } F+                   H+              C2
      { KC2 H+ F@ F/         } F+ } F/ }           ----  +  1   + -----
  ALPHA.C1 F! ;                                     K               H+
                                                     C1

: CALC:A.C2 ( --- )                                             K
  KC2 H+ F@ F/ ALPHA.C1 F@ F*                                    C2
  ALPHA.C2 F! ;                         ALPHA  :=  ALPHA   (---)
                                             C2          C1    H+

: CALC-ALPHAS ( --- )
           CALC:A.P2
  CALC:A.P1 CALC:A.P3
  CALC:A.C1 CALC:A.C2 ;

-->


------=======****** 18 ******=======------
\ CALC:CT                               -->

: CALC:CT   ( -- )                      CT :=   ALK -  P ALPHA
  ALK F@ PT F@ ALPHA.P2 F@ F* F-                        T     P2
  ALPHA.C1 F@ F/ CT F! ;                        ----------------
                                                    ALPHA
-->                                                      C1




                                        ( ORIGINAL, NOT REALLY NEEDED )

                                        CT :=
                                               K
                                                W
                                        ALK - --- - P ALPHA  - 2P ALPHA  + (H+)
                                             (H+)     T     P2     T     P3
                                        ----------------------------------------

                                               ALPHA   + 2ALPHA
                                                    C1          C2
```

```
------======****** 15 ******======------
\ CALC:A.P1                             -->

: CALC:A.P1 ( --- )                                 H+
  H+ F@ KP2 F/ ALPHA.P2 F@ F*           ALPHA  :=  ---- (ALPHA   )
  ALPHA.P1 F! ;                              P1     K          P2
-->                                                  P2
```

```
------======****** 16 ******======------
\ CALC:A.P2   CALC:A.P3                 -->

: CALC:A.P2 ( --- )                                              1
  { 1.0                                 ALPHA   :=   ---------------------------
    { { 1.0                    }             P2                     2    K
      { H+ F@ KP2           F/  } F+                 H+    (H+)      P3
      { { H+ F@ 2.0 F↑   }                       1 + ---- + ------ + ----
        { KP1 KP2 F*     } F/  } F+                 K      K  K
      { KP3 H+ F@           F/  } F+ }               P2     P1 P2    H+
                                    F/ }
  ALPHA.P2 F! ;                                     K
                                                     P3
                                        ALPHA  :=  ----- (ALPHA   )
: CALC:A.P3 ( --- )                          P3      H+        P2
  KP3 H+ F@ F/ ALPHA.P2 F@ F*
  ALPHA.P3 F! ;

-->
```

```
------======****** 19 *************=====------
\ CALCULATE SPECIES DISTRIBUTION        -->  --
                                           CO       := C   ALPHA
: CALC:CO3--  ( --- )                        3           T        C2
  { CT F@ ALPHA.C2 F@ F* } CO3--   F! ;
                                                -
                                           HCO      := C   ALPHA
: CALC:HCO3-  ( --- )                          3         T        C1
  { CT F@ ALPHA.C1 F@ F* } HCO3-   F! ;
                                               ---
                                           PO       := P   ALPHA
: CALC:PO4--- ( --- )                        4           S        P3
  { PS F@ ALPHA.P3 F@ F* } PO4---  F! ;
                                                --
                                           HPO      := P   ALPHA
: CALC:HPO4-- ( --- )                          4         S        P2
  { PS F@ ALPHA.P2 F@ F* } HPO4--  F! ;
                                                 -
                                           H PO     := P   ALPHA
: CALC:H2PO4- ( --- )                       2  4         S        P1
  { PS F@ ALPHA.P1 F@ F* } H2PO4-  F! ;
                                              -
                                           OH       := KW
: CALC:OH-     ( --- )                                 ----
  KW H+ F@ F/ OH- F! ;                                  H+


-->


-----======****** 20 ************======------
\ CALC-SPECIES  BACKUP

: CALC-SPECIES ( --- )
  CALC:CO3--  CALC:HCO3-
  CALC:PO4--- CALC:HPO4--
  CALC:H2PO4- CALC:OH- ;

: BACKUP
  CO3-- F@ CO3--0  F! HCO3- F@ HCO3-0 F!
  PO4--- F@ PO4---0 F! OH-  F@ OH-0   F!BACKUP SAVES THE INITIAL ALPHA AND
  HPO4-- F@ HPO4--0 F! H+   F@ H+0    F!
  H2PO4- F@ H2PO4-0 F!                  SPECIES DISTRIBUTION VALUES.
  ALPHA.C1 F@ ALPHA.C10 F!
  ALPHA.C2 F@ ALPHA.C20 F!              ALL OF THE VALUES ENDING WITH
  ALPHA.P1 F@ ALPHA.P10 F!
  ALPHA.P2 F@ ALPHA.P20 F!              "0"
  ALPHA.P3 F@ ALPHA.P30 F! ;


-->
```

```
-----=====****** 21 ******=====-----
\ EXCESS.ALUM? CALC:PS0

: EXCESS.ALUM?
  ALT F@
  R F@
  PT F@ 1.0E-4 F+ F*   F>  ;

: CALC:PS0
  PT F@ ALT F@ R F@ F/ F-

  0.0 FMAX ( RESTRICT TO BE >= 0 )

  PS0  F! ;

-->
```

THERE IS EXCESS ALUM IF

$$AL_T > R\ (P_T + 10^{-4})$$

$$P_{S0} := PT - \frac{AL_T}{R}$$

BUT IN CASE THE RESULT IS LESS THEN ZERO, P_{S0} IS SET TO BE EQUAL TO ZERO.

```
-----=====****** 22 ******=====-----
-->
```

```
-----=====****** 23 ******=====------
-->
```

```
-----=====****** 24 ******=====------
\ CALC:CA.1
                                           SINGLE-PRECIPITATE CALCULATION OF CA

: CALC:CA.1 ( --- )
   R F@ 3.0 F* F2- ALPHA.P20 F@ F*         CA :=
   R F@ 3.0 F* F1- ALPHA.P10 F@ F* F+
   R F@ F/  ALT F@ F*
  CA F! ;                                  (3R-2)(ALPHA    )+(3R-1)(ALPHA    )
                                                       P20              P10
                                           -------------------------------- (AL  )
( CALLED WHEN THERE IS 1 PRECIPITATE )                    R                     T
-->
```

```
-----=======****** 25 **********======------
\ F1(H)                                    FIRST F(H) CALCULATION

: F1(H)  ( --- FP )
  CALC-ALPHAS
  CALC-SPECIES
                                                           -
                                           F(H) := C  + (OH ) + 2(CO     )
  ( WE NEED ALPHA VALUES AND SPECIES                A                  3
    DISTRIB BEFORE WE CAN CALCULATE. )
                                                        -          -
  CA F@                                          + (HCO  ) + (HPO    )
  OH- F@ F+                                             3         4
  CO3-- F@ F2* F+
  HCO3- F@ F+                                    - H+ - C
  HPO4-- F@ F+                                          I
  H+ F@ F-
  CI F@ F- FDUP SOLUTION F! ;

-->
```

```
-----=======****** 26 **********======------
\ CALC:H+.1
                                           TO CALCULATE H+, WE SET F(H) TO BE
: CALC:H+.1                                F(X), AND H+ TO BE THE ROOT.
  [' ] F1(H) IS F(X)                       THEN WE CALL GET-ROOT AND STORE
  [' ] H+    IS ROOT                       THE RESULT IN H+.
  GET-ROOT H+ F! ;

-->
```

```
-----=======****** 27 ******=======------
\ CALC-ALUMINUMS
: CALC:A.A0   ( -- )                    ALUMINUM ALPHA VALUE CALCULATIONS.
  { { 1.0 }
    { *K1 H+ F@ F/ } F+
    { { *K1 *K2 F* }                    ALPHA   :=
      { H+ F@ 2.0 F↑ } F/ } F+               A0
    { { { *K1 *K2 F* } *K3 F* }
      { H+ F@ 3.0 F↑ } F/ } F+             *K1  *K1*K2   *K1*K2*K3  *K1*K2*K3*K4

    { { { *K1 *K2 F* }                  1+ -- + ------ + --------- + ----------
        { *K3 *K4 F* } F* }                         2         3           4
      { H+ F@ 4.0 F↑ } F/ } F+ }           H+     H+        H+          H+
   F1/X ALPHA.A0 F! ;
: CALC:A.A1 ALPHA.A0 F@ *K1 F* H+ F@ F/ ALPHA      (ALPHA   ) (*K1/H+)
  ALPHA.A1 F! ;                              A1 :=       A0
: CALC:A.A2 ALPHA.A1 F@ *K2 F* H+ F@ F/
  ALPHA.A2 F! ;                         ALPHA   := (ALPHA   ) (*K2/H+)
: CALC:A.A3 ALPHA.A2 F@ *K3 F* H+ F@ F/      A2          A1
  ALPHA.A3 F! ;
: CALC:A.A4 ALPHA.A3 F@ *K4 F* H+ F@ F/ ALPHA   := (ALPHA   ) (*K3/H+)
  ALPHA.A4 F! ;                              A3          A2
: CALC-ALUMINUMS ( -- )
   CALC:A.A0 CALC:A.A1                  ALPHA   := (ALPHA   ) (*K4/H+)
   CALC:A.A2 CALC:A.A3 CALC:A.A4 ; -->       A4          A3

-----=======****** 28 ******=======------
\ A. B FOR PHOSPHATE RESIDUAL           A, B, C, AND D ARE THE COEFFECIENTS
FVARIABLE A FVARIABLE B                 FOR THE P  EQUATION.
FVARIABLE C FVARIABLE D                          F
: CALC:A
  { { { H+ F@ 2.0 F↑ }                           2
      { KP2 KP3 F*   } F/ }                    H+      H+    ✓
    { { H+ F@        }                  A :=  ------ + ---
      { KP3          } F/ } F+ }              K  K     K
  A F! ;                                       P2 P3    P3
: CALC:B
  { { R F@ { FDUP F1- } FSWAP F/ }

                                                               (5R-3)/R
    { { K  { KSO R F@                                   K(K  1/R)(H         )
               F1/X F↑ } F*                   R-1      SO
           { H+ F@ { 5.0 R F@ F* 3.0 F- B := (---) (--------------------)
          R F@ F/ } F↑ } F* }                  R     (K 3R-3/R)(K   )(K   )
      { { KW                                               W         P2   P3
          { R F@
            { { FDUP 3.0 F* } 3.0 F- }
         FSWAP F/ } F↑ }
        { KP2 KP3 F* } F* } F/ } F* }
  B F! ;
-->
```

```
-----======****** 29 ******======------
\ C. D FOR PHOSPHATE RESIDUAL
                                                               3R-3/R
: CALC:C                                          (K   1/R) (H+      )
  { { R F@ F1/X                   }            1    SO
    { { KSO FOVER   F↑  }                 C := (-) (------------------)
      { H+ F@ { R F@ { { FDUP 3.0 F* }         R         3R-3/R
        3.0 F- } FSWAP                                (K        )
                F/ } F↑ } F*                            W
      { KW     { R F@ { { FDUP 3.0 F* }
        3.0 F- } FSWAP
               F/ } F↑  } F/       } F*      (1 + A   + A   + A   + A   )
    { 1.0                                             A0    A1    A2    A3
      { ALPHA.A0 F@          } F+
      { ALPHA.A1 F@          } F+
      { ALPHA.A2 F@          } F+
      { ALPHA.A3 F@          } F+ } F* }
  C F! ;                                  D := P  - (AL )
                                               T      T
: CALC:D                                          -----
  { PT F@                                           R
    { ALT F@ R F@ F/ } F- }
  D F! ;
-->

-----======****** 30 ******======------
\ F(PO4---)                               F(PO4---)  :=

: F(PO4---)  (    --- F[PO4---] )                        R-1         -1
  (PO4---) F@                                            ---         ---
  A F@ FOVER F*           \ PF A*PF                       R           R
                                                AP  + BP        - CP         - D
  FOVER R F@ FDUP 1.0 F-                          F     F            F
  FSWAP F/ F↑
  B F@ F* F+              \ PF A*+B*

  FSWAP R F@ F1/X FNEGATE F↑
  C F@ F* F-              \ A*+B*-C*

  D F@ F-                 \ A*+B*-C*-D*
  FDUP SOLUTION F! ;

-->
```

```
------======****** 31 ******======------
\ CALC:(P04---)

: CALC:(P04---)  ( -- )                 TO CALCULATE (P04---), WE FIRST
  CALC:A CALC:B CALC:C CALC:D
  ['] F(P04---) IS F(X)                 CALCULATE THE CONSTANT COEFFECIENTS
  ['] (P04---)  IS ROOT
  GET-ROOT (P04---) F! ;                A, B, C, AND D.  THE WE SET F(X) TO

-->                                     CALL F(P04---) AND SET THE ROOT TO BE

                                        (P04---), AND CALL THE EQUATION-SOLVER.
```

```
------======****** 32 ******======------
\ CALC:PS.TRIAL                         TRIAL P   :=
: CALC:PS.TRIAL   ( -- )                       S
  { { { { H+ F@ KP3 F/ }                           {              2   }
        { { H+ F@ 2.0 F↑ }                         { H+       (H+)    }
          { KP2 KP3 F* } F/ } F+ }      (P04---) * {----- +  ------   }
          (P04---) F@ F* }                         { K       K  K     }
                                                   {  P3      P2 P3   }
    { { { K }                                      {                  }
        { KS0 R F@ F1/X F↑ } F*
        { H+ F@ { 2.0                                                           R-1
            { { { R F@ 3.0 F* } 3.0 F- }         1         3R-3/            ---
               R F@ F/ } F+ } F↑ } F*            -      2+    /R             R
        { (P04---) F@                    K * K  R *  (H+)          * (P04---)
               { R F@ F1- R F@ F/ }             S0
                    F↑ } F* }           + -----------------------------------
    { { KP2 } { KP3 } F*                                3R-3/
      { KW { { { 3.0 R F@ F* } 3.0 F- }     K  K  K   /R
          R F@ F/ } F↑ } F* } F/ } F+ }      P2 P3 W
  PS.TRIAL F! ;

: CALC-RESIDUAL
  CALC:(P04---)
  CALC:PS.TRIAL ;   -->
```

```
------=======****** 33 ******=======------
\ RESIDUAL.OFF? RECALC.PS

: RESIDUAL.OFF?
  PS.TRIAL F@ PS F@ F/ ( RATIO )
  F1- ( NOW HOPEFULLY IN RANGE -.1 +.1)
  FABS 0.1 F> ; ( TRUE IF INACCURATE )

: RECALC:PS
  PS F@ PS.TRIAL F@ F+ 2.0 F/ PS F! ;


-->
```

RESIDUAL.OFF? RETURNS TRUE IF WE ESTIMATED WRONGLY ABOUT THE PRECIPITATION, MEANING THAT WE SHOULD CALCULATE FOR ALUMINUM HYDROXIDE PRECIPITATION.

FALSE OTHERWISE.

RECALC:PS TRYS A NEW VALUE OF P_S

BY TAKING THE AVERAGE OF THE P_S VALUE

JUST CALCULATED WITH THE PREVIOUS P_S

```
------=======****** 34 ******=======------
-->
```

```
-----=====****** 35 ******=====------
\ ANY.PRECIPITATE?

: ANY.PRECIPITATE?
  { { { ALT   F@ ALPHA.A0 F@ F* }
        R F@ F^        }
    { PT F@          } F*
    {   ALPHA.P3 F@ } F*
    { { KW H+ F@ F/ }
      { { R F@ 3.0 F* } 3.0 F- }
              F^ } F* }


  KSO F> ;

-->
```

THERE IS ONE PRECIPITATE, NOT ZERO. IF

$$\left[(AL_{T})(ALPHA_{A0})\right]^{R}(P_{T})(ALPHA_{P3})\left(\frac{K_{W}}{H+}\right)^{3R-3}$$

IS GREATER THAN K_{SO}

```
-----=====****** 36 ******=====------
\ CALC:CI

: CALC:CI    ( --- )
  { { HPO4--0 F@          }
    { CO3--0  F@ F2*      }    F+
    { HCO3-0  F@          }    F+
    { OH-0    F@          }    F+
    { H+0     F@          }    F- }
  CI F! ;

-->
```

CALCULATION OF C_{I}

$$C_{I} := HPO4^{--}_{0} + 2(CO3^{--}_{0}) + HCO3^{-}_{0}$$

$$+ OH^{-}_{0} - (H+_{0})$$

```
------======****** 37 ******======------
\ F0(H)                                  THE ZERO-PRECIPITATE CALCULATION OF H+

: F0(H) ( -- FP )
  CALC-ALPHAS CALC-ALUMINUMS             F(H) :=  C   + (H+) - (OH-)
  { CI F@                                          I
    H+  F@ F+
    OH- F@ F-
    { CT F@                              + C  ( ALPHA   + 2(ALPHA  ))
      { ALPHA.C1 F@                         T         C1            C2
        ALPHA.C2 F@ F2* F+ } F* } F-
    { PT F@
      { ALPHA.P2 F@                      + P  ( ALPHA   + 2(ALPHA  ))
        ALPHA.P3 F@ F2* F+ } F* } F-        T         P2            P3
    { ALT F@
      { ALPHA.A1 F@
        ALPHA.A2 F@ F2* F+               + AL  ( ALPHA   + ALPHA   + ALPHA
        ALPHA.A3 F@ 3.0 F* F+               T          A0        A1         A2
        ALPHA.A4 F@ 4.0 F* F+ }
                              F* } F- }        + ALPHA   )
  FDUP SOLUTION F! ;                                 A3


-->

------======****** 38 ******======------
\ CALC:H+.0

: CALC:H+.0                              THIS IS THE CALCULATION FOR H+ WHEN
  [' ] F0(H) IS F(X)
  [' ] H+    IS ROOT                     THERE ARE NO PRECIPITATES.  IT IS
  GET-ROOT H+ F! ;
                                         CALCULATED BY SETTING F(X) TO

-->                                      CALL F0(H) AND BY SETTING H+ TO BE

                                         THE ROOT VARIABLE.
```

```
-----=====****** 39 ***********======------
\ CALC:PH.FINAL
                                                          -PH
: CALC:PH.FINAL                               SINCE H+ = 10    , PH := -LOG(H+)
  H+ F@ FLOG FNEGATE PH F! ;

-->


                                              DON'T YOU AGREE?
```

```
-----=====****** 40 ***********======------
\ CALC:ALK.FINAL

: CALC:ALK.FINAL
  HCO3- F@ CO3-- F@ F2* F+ H2PO4-             FINAL ALKALINITY CALCULATION:
  F@ F+ HPO4-- F@ F2* F+
  OH- F@ F+ H+ F@ F-                          ALK :=
  ALK F! ;
                                                 -         --        -          -
-->                                           HCO    + 2(CO    ) + H PO    + 2(HPO  )
                                                 3         3       2  4          4

                                                 -
                                              + OH   - (H+)
```

```
-----=======****** 43 ******=======------
\ F2(H)
: F2(H)  ( --- FP )
  { { CI F@ FNEGATE }
    { H+ F@ } F-
    { { { { H+ F@ KC1 F/ F1+ }
      { KC2 H+ F@ F/ } F+ F1/X }
        { KC2 F2* H+ F@ F/ F1+ }
          F* } CT F@ F* } F+
    { CA F@ } F+ } FDUP SOLUTION F! ;
-->
```

CA.2?

```
2-PRECIP CALCULATION OF H+
         F(H+) := -C   - (H+) + C  +
                   I2          A2
   ( (    1       )  (    2KC )  )
 C ( ( --------   )  (        2) )
  T( ( H+     K   ) * (1 + ----)  )
   ( ( -- +1+   C2)  (     H+ )  )
     ( K       ---)  (        )
     (  C1      H+)  (        )

*************************************
                 4      R    3R-3
THIS PART     (H+ )(*KSO )(KW     )
OMMITTED.  +  --------------------
                 K   K
                  P3  SO

           (     4           2      )
         3 (---------- - -----------)
*K   (H+)  (      4            2    )
  SO       (    H+          H+     )
               ----        ------
            *K1*K2*K3*K4   *K1*K2
```

```
-----=======****** 44 ******=======------
\ CALC:H+.2

: CALC:H+.2
  ['] F2(H) IS F(X)
  ['] H+    IS ROOT
  GET-ROOT  H+ F! ;

-->
```

```
SIMILAR TO THE FIRST CALCULATION OF H+.

2CALC:H+ SETS F(X) TO BE F2(H)

SETS THE ROOT TO BE H+

GETS THE ROOT AND STORES IT IN H+
```

```
-----======****** 45 ******=======------
\ CALC: (PO4---).FINAL CALC:PS.FINAL    2 PPT: FINAL CALCULATION OF (PO4---) IS:

: CALC:(PO4---).FINAL
  KSO                                                  KSO
  *KSO R F@ F↑                          (PO4---) := -----------------
  KW R F@ 3.0 F* 3.0 F- F↑                              R  3R-3   3
  F* H+ F@ 3.0 F↑ F*                                *KSO KW    (H+)
  F/
  (PO4---) F! ;

                                        FINAL 2-PPT CALCULATION OF PS IS:

: CALC:PS.FINAL ( --- )                              [           2            5]

  { (PO4---) F@                                      [ H+   (H+)   K(*KSO)(H+) ]

    { { H+ F@ KP3 F/        }           P := (PO4---)[--- + ----- + -----------]

      { { H+ F@ 2.0 F↑ }                 S           [KP    KP KP    KP KP     ]

        { KP2 KP3 F*   } F/ } F+                        3     2  3     2  3
      { { K *KSO F*
          H+ F@ 5.0 F↑
          F*           }
        { KP2 KP3 F*   } F/ } F+ } F* }
  PS F! ;

-->


-----======****** 46 ******=======------
\ PATH VECTOR, BOOLEAN VARIABLES.
                                        THESE WORDS ARE USED TO SIGNIFY
DEFER PATH                              WHICH "PATH" WAS TAKEN THROUGH THE
                                        PROGRAM-- NO PRECIPITATES, ONE, TWO,
: 0-PRECIP                               OR ONE MODIFIED TO TWO.
  ." (0 PRECIP)" ;
: 1-PRECIP                              PATH IS A DEFERRED WORD WHICH IS SET
  ." (1 PRECIP)" ;                      IN MAIN.CALC TO RUN ANY OF THE WORDS
: 2-PRECIP                              0-PRECIP, 1-PRECIP, 2-PRECIP,
  ." (2 PRECIP)" ;                      OR 1>2-PRECIP.
: 1>2-PRECIP
  ." (1>2 PPT) " ;

VARIABLE SOLIDS   VARIABLE PRINTER
VARIABLE WAITING VARIABLE FORCE-2
VARIABLE ZOOM    VARIABLE DZOOM

-->
```

MAIN.CALC SETS UP PATH TO RUN THE
APPROPRIATE WORD.

```
-----======****** 49 ******======------
-->
```

```
-----=======****** 50 *******======------
\ MAIN.CALC                                  1) CONVERT INPUT VALUES.  2) SET PS TO
: MAIN.CALC ( --- ) CONVERT-INPUTS          EQUAL PT. 3) CALCULATE ALPHAS, CT,
  PT F@ PS F! CALC-ALPHAS CALC:CT           SPECIES DISTRIBUTION. 4) SAVE ALPHAS
  CALC-SPECIES BACKUP FORCE-2 @             AND SPECIES. 5) IS THERE EXCESS ALUM?
  EXCESS.ALUM? OR                           OR IS FORCE-2 ON?
  NOT IF [' ] 1-PRECIP IS PATH              6) IF NOT, ANNOUNCE ONE PRECIP. 7) CAL-
    CALC:PS0 PS0 F@ PS F!                   CULATE PS0, STORE PS0 INTO PS. 8) CALCU-

    CALC:CI   CALC:CA.1                     LATE CI AND CA (WITH THE 1-PPT FORMULA)
    CALC:H+.1 CALC-ALUMINUMS                9) IN A LOOP, CALCULATE H+ WITH
    CALC-RESIDUAL RECALC:PS                 SUCCESSIVE APPROXIMATIONS. FIND THE AL
    BEGIN CALC:H+.1 CALC-ALUMINUMS          ALPHAS, AND CALCULATE PS. WHILE THE
      CALC-RESIDUAL                         RESIDUAL IS INACCUARATE, TAKE THE MEAN
      RESIDUAL.OFF?    RECALC:PS            AND REPEAT THE LOOP. 10) NOW CHECK TO
    NOT UNTIL                               SEE IF THERE IS INDEED ANY PRECIPITATE.
    ANY.PRECIPITATE? NOT                    11) IF THERE ISN'T, ANNOUNCE ZERO PPTS.
    IF [' ] 0-PRECIP IS PATH                12) CALCULATE CI, H+, AND A FINAL PH.
      CALC:CI                               13) STORE PT INTO PS, CALCULATE FINAL
      CALC:H+.0 CALC:PH.FINAL               ALKALINITY, AND EXIT THIS ROUTINE.
      PT F@ PS F! ( CALC:ALK.FINAL )        14) (CONTINUING WITH 1 PPT) CHECK IF
      0.0 SLUDGE F! EXIT                    SOLUBILITY IS EXCEEDED. IF SO, ANNOUNCE
    THEN SOLUBILITY.EXCEEDED?               THERE IS 1->2 PPTS, AND LEAVE A "TRUE".
    IF [' ] 1>2-PRECIP IS PATH   TRUE       15) ELSE LEAVE "FALSE" AND MAYBE CALC
    ELSE ?CALC:SLUDGE/1 FALSE THEN -->      THE SOLIDS... WE WON'T DO 2-PPT..
```

```
-----======****** 51 *****=======------
\ MAIN.CALC, CONTINUED        F.        16) OTHERWISE, (FROM ABOVE, MEANING
                                         THAT THERE WAS EXCESS ALUM) ANNOUNCE
  ELSE [']  2-PRECIP IS PATH   TRUE     THAT THERE ARE 2 PRECIPITATES AND LEAVE
  THEN                                  A "TRUE".
                                        17) IF THE FLAG LEFT ON THE STACK
  IF CALC:CI    CALC:CA.2 CALC:H+.2     IS TRUE, THEN WE DO THE 2-PPT CALC.
    CALC-ALPHAS CALC-SPECIES            IF SO...
    CALC:(PO4---).FINAL CALC:PS.FINAL   18) CALCULATE CI AND CA, H+
    ?CALC:SLUDGE/2                      19) CALCULATE ALPHAS AND SPECIES
  THEN                                  DISTRIBUTION. 20) CALCULATE A FINAL PS.
  CALC:ALK.FINAL CALC:PH.FINAL ;        21) POSSIBLY CALCULATE THE SOLIDS
                                        22) IN EITHER CASE (1 OR 2 PPTS)
                                          CALCULATE A FINAL ALKALINITY AND PH.


: F. ( SMALLER PRECISION HERE )
  1000.0 F* FROUND 1000.0 F/ F. ;


-->
```

```
-----======****** 52 *****=======------
\ SOFT 70 LOAD, RANGE VARIABLES
                                        HERE WE LOAD THE SCREEN THAT BRINGS
137 LOAD ( GET SOFT SEVENTY )           UP SOFT-SEVENTY

FVARIABLE ALK.INITIAL
FVARIABLE ALK.FINAL
FVARIABLE ALK.INC                       THESE ARE THE RANGE VARIABLES THAT

FVARIABLE PH.INITIAL                    ARE SET UP FROM "RANGES"
FVARIABLE PH.FINAL
FVARIABLE PH.INC

FVARIABLE PHOS.INITIAL
FVARIABLE PHOS.FINAL
FVARIABLE PHOS.INC

FVARIABLE DOSE.INITIAL
FVARIABLE DOSE.FINAL
FVARIABLE DOSE.INC

-->
```

```
-----========****** 53 ******========------
-->        \ PRINT-VALUES                     TAB SETS APPLE LOCATION 36. WHICH HOLDS
                                              THE HORIZONTAL TABULATION.
: TAB 36 C! ;                                 0 TAB IS THE LEFT EDGE OF THE SCREEN.

: PRINT-VALUES
  CR ." **************  " PATH CR
(  CR ." CO3--:" CO3-- F@ F.
   25 TAB ." HCO3-:" HCO3- F@ F.
   CR ." PO4---:" PO4--- F@ F.
   25 TAB ." HPO4--:" HPO4-- F@ F.
   50 TAB ." H2PO4-:" H2PO4- F@ F.
   CR ." OH-:" OH- F@ F.
)  CR ." ALK:" ALK F@ 50000.0 F* F.
   CR 25 TAB ." PH: " PH F@ F.
   50 TAB ." PT: " PT F@ F.
   CR ." PS: " PS  F@ 31000.0 F*
   ( CONVERT MOLES/LITER TO
     MG/LITER AS P )  F. ." MG/L"
   CR CR ;

-->


-----========****** 54 ******========------
-->
```

```
-----=======****** 55 ******=======------
-->        \ ASKER
: ASKER   HOME
  ." ALUM DOSE   (MG/L) ?"
  INPUTF# ALUM.DOSE(MG/L) F! CR
  ." ALKALINITY  (MG/L) ?"
  INPUTF# ALKALINITY(MG/L) F! CR
  ." PHOSPHATE CONCENTRATION (MG/L)"
  CR ." ?"
  INPUTF# PHOSPHATE.CONC(MG/L) F! CR

( ." PH ?"
  INPUTF# PH F! CR
  ." REACTION RATIO OF 1.4? " QUERY-Y/N
  IF 1.4
  ELSE CR ." REACTION RATIO ?"
    INPUTF# CR
  THEN R F!                        )

  1.4 R F! 8.5 PH F!
  MAIN.CALC
  PRINT-VALUES ;

-->

-----=======****** 56 ******=======------
\ PRINT-FOR-FINDER

: PRINT-FOR-FINDER
  CR
  10 SPACES

 ."  Alk = "
        ALKALINITY(MG/L) F@ F.
 ."  Phosphate = "
        PHOSPHATE.CONC(MG/L) F@ F.
 ."  pH: initial =  "
        PH.INPUT F@ F. ;

-->




( LOWERCASE WORDS HERE )
```

```
------======****** 57 ******======------
\ 1-CYCLE

: 1-CYCLE
   MAIN.CALC
 CR SPACE DOSE-NAME ." DOSE = "
        ALUM.DOSE(MG/L) F@ F.
 ."   ALK = "
        ALKALINITY(MG/L) F@ F.
 ."   PHOSPHATE = "
        PHOSPHATE.CONC(MG/L) F@ F.
 ."   PH: INITIAL =  "
        PH.INPUT F@ F. 5 SPACES    CR
 ."   FINAL PH = "
        PH F@ F.
 ." FINAL ALK = "
        ALK F@ 50000.0 F* F.
 ."   PS = " PS F@ 31000.0 F* F.
 PATH
 SOLIDS @ IF CR ." SOLIDS(MG/L) = "
   SLUDGE F@ F.
 THEN CR ;

-->

------======****** 58 ******======------
\ PS.SCALE  DOSE.SCALE

: PS.SCALE ( --- Y-COORD )
  PS F@ 31000.0
  F*
  DZOOM @ IF 0.1 ELSE ZOOM @ IF 1.0
  ELSE 10.0 THEN THEN
  F/ 150.0 F* FROUND 32000.0 FMIN
  ABSOLUTE 149 SWAP - 10 + 0 MAX
  ( 159 MIN ) ;

: DOSE.SCALE ( --- X-COORD )
  ALUM.DOSE(MG/L) F@ DOSE.INITIAL F@ F-
  DOSE.FINAL F@ DOSE.INITIAL F@ F-
  F/ ( NOW A FRACTION )
  269.0 F* ( NOW IN HI-RES RANGE )
  ABSOLUTE 10 + ;

-->

: PH.SCALE ( --- Y-COORD )
  PH F@ 10.0 F/ 150.0 F* FROUND
  ABSOLUTE 149 SWAP - 10 + 0 MAX ;
```

```
------======****** 59 ******======------
\ SETUP-GRAPH
VARIABLE FIRST-POINT
: SETUP-GRAPH       FIRST-POINT ON
  BLACK2 GRAPHICS WHITE COLOR INVOKE
  10 10 POSN 279 10 LINE 279 159 LINE
  10 159 LINE 10 10 LINE ( FRAME )
  160 10 DO ( SIDE TICKS )
    11 I POSN 13 I LINE
   276 I POSN 278 I LINE
  15 +LOOP      101 0 DO ( HORIZ TICKS)
    I 269 100 */ 10 + DUP 11 POSN DUP
    13 LINE DUP 156 POSN 158 LINE
  10 +LOOP 10 1 DO 1   I 2*   AT
  10 I - 1 .R LOOP
  DOSE.INITIAL F@ ABSOLUTE 0 0 AT .
  DOSE.FINAL F@ ABSOLUTE  64 0 AT 5 .R
  20 0 AT ." SCALE 0 - " DZOOM @ IF
  ." .1" ELSE ZOOM @ IF ." 1" ELSE
  ." 10" THEN THEN
  PRINTER @ IF ."  PRINTER" THEN
  10 SPACES DOSE-NAME ." MODEL"
  20 34 C! HOME PRINTER @ IF
  3 PR# 30 EMIT THEN ;  -->

------======****** 60 ******======------
\ RANGES

: ?STEP ( FP1 FP2 --- FP3 ) F= IF 1.0
  ELSE CR ." STEP?" INPUTF# CR THEN ;
: RANGES TEXT HOME CR CR DOSE-NAME
  ." MODEL...." CR CR
  ." INITIAL ALKALINITY?" INPUTF# FDUP
  ALK.INITIAL F! CR ." FINAL ALK?"
  INPUTF# FDUP ALK.FINAL F! ?STEP
 ALK.INC F! HOME ." INITIAL PH?" INPUTF#
 CR FDUP PH.INITIAL F! ." FINAL PH?"
 INPUTF# FDUP PH.FINAL F! ?STEP
 PH.INC F! HOME ." INITIAL PHOSPHATE?"
 INPUTF# FDUP PHOS.INITIAL F! CR
 ." FINAL PHOS?" INPUTF# FDUP PHOS.FINAL
 F! ?STEP PHOS.INC F!
 HOME ." INITIAL DOSE?" INPUTF# FDUP
 DOSE.INITIAL F! CR ." FINAL DOSE?"
 INPUTF# FDUP DOSE.FINAL F! ?STEP
  DOSE.INC F! HOME  ;

-->
```

```
-----=======****** 61 ******=======------
\ SCALE  DESCALE

50.0 FCONSTANT SCALAR
: SCALE ( FP --- N )
  SCALAR F* ABSOLUTE ;

: DESCALE ( N --- FP )
  FLOAT SCALAR F/ ;

( WE MULTIPLY THE LOOPING BOUNDS
  BY A SCALAR FOR THE LOOP SETUP.
  MULTIPLYING BY FIFTY GIVES US
  PRECISION OF .02 AND A RANGE OF
  ROUGHLY +- 650 ON OUR RANGES, WHICH
  IS JUST DUCKY FOR THIS APPLICATION. )


-->
```

```
-----=======****** 62 ******=======------
\ 1-PLOT

VARIABLE OLDX VARIABLE OLDY
: 1-PLOT (   --    )
   1-CYCLE
   PH F@ 3.0 F> IF
     DOSE.SCALE
     PS.SCALE
     FIRST-POINT @
     IF
        2DUP OLDY ! OLDX ! PLOT
       FIRST-POINT OFF
     ELSE OLDX @ OLDY @    POSN
       2DUP OLDY ! OLDX !  LINE
     THEN
   THEN ;

-->
```

USER INSTRUCTIONS FOR PHOSPHATE PRECIPITATION MODEL

SET UP

The phosphate precipitation model is written for an Apple II+ or Apple IIe microcomputer with a printer in slot 3, and one disk drive in slot 6.

To start the program, turn the computer off, insert the disk in the disk drive and turn the computer on. The disk drive light should come on and the drive whir while the program is being loaded into memory. When the light goes off a help screen will appear on the monitor.

Select the Ferric Chloride or Alum precipitation model by typing ALUM or IRON then hitting the return key. After typing one of these words, the value of r (the reaction ratio) is automatically set to its appropriate default value: 1.2 for the iron; 1.4 for alum. After setting ALUM or IRON, the value of r can be changed to some other value until the next time the program is booted or until the next time IRON or ALUM is typed. To do this, type in the new value for r, a space, the letter R, another space, then F!, then the return key. For example, this will store 1.5 into R.

```
1.5 R F!
```

ENTERING DATA

The next step is to enter the data for the cases to be run. The model needs to know the initial alkalinity (in mg/l as $CaCO_3$), initial pH, initial soluble phosphate (in mg/l as P), and the coagulant dose (in mg/l as $FeCl_3$ or Alum). To enter this information type RANGES and hit the return key.

The program is set up so that more than one case can be run at one time. To do this it asks for a range of input values and the increment between them. For example, after typing RANGES and hitting the return key the program prompts for "Initial Alkalinity?". Enter the lowest value of alkalinity that you want to try. It then asks for Final Alkalinity?". Enter the highest value of alkalinity you want to try. It then asks for "Step?". Enter the increment. For example, if you want to look at the range of alkalinity between 100 and 200 the screen would look like this:

```
INITIAL ALKALINITY?   100
FINAL ALK? 200
STEP? 10
```

If you want to look at just one alkalinity the screen would look like this:

```
INITIAL ALKALINITY?  100
FINAL ALK?  100
STEP? 0
```

The procedure is the same for entering the data for the other inputs.

If you enter an incorrect number you can change it by backspacing and reentering before you hit return. If you hit return before you notice the error hit the control key and the reset key at the same time and start over.

CHOOSING OUTPUT FORMAT

The next step is to choose the output format. The following options are available:

1. Printed output.

2. A graph displayed on the screen with a range of soluble phosphate residual of:
   a. 0 - 10
   b. 0 - 1
   c. 0 - 0.1.

To enable or disable the printing mode, use:

PRINTER ON   or

PRINTER OFF

The program is set up for a printer in slot 3. When the model is actually run, output will be sent to the printer if PRINTER has been turned ON.

Changing the Vertical Scale on the Graph

In normal operation, the horizontal axis of the graph will range from a phosphate residual of 0 to a residual of 10. Since it is often desirable to view the graph more precisely at small doses, the swithes ZOOM and DZOOM (double-zoom) can be used to alter the scale from 0 to 1 (when ZOOM is on) or from 0 to 0.1 (when DZOOM is on) To turn on or off, use:

ZOOM ON or
ZOOM OFF or

DZOOM ON or
DZOOM OFF

Waiting for User Response After Each Graph

A switch called WAITING exists in the program so that when it is turned ON, the microcomputer will wait for the user to press a key after each graph or set. To set the state of WAITING, use:

WAITING ON or
WAITING OFF

Plotting

The program is set up to always show the results plotted on the screen as the program is being run.

RUNNING THE MODEL

To start the model type:

PLOTTER then hit the return key.

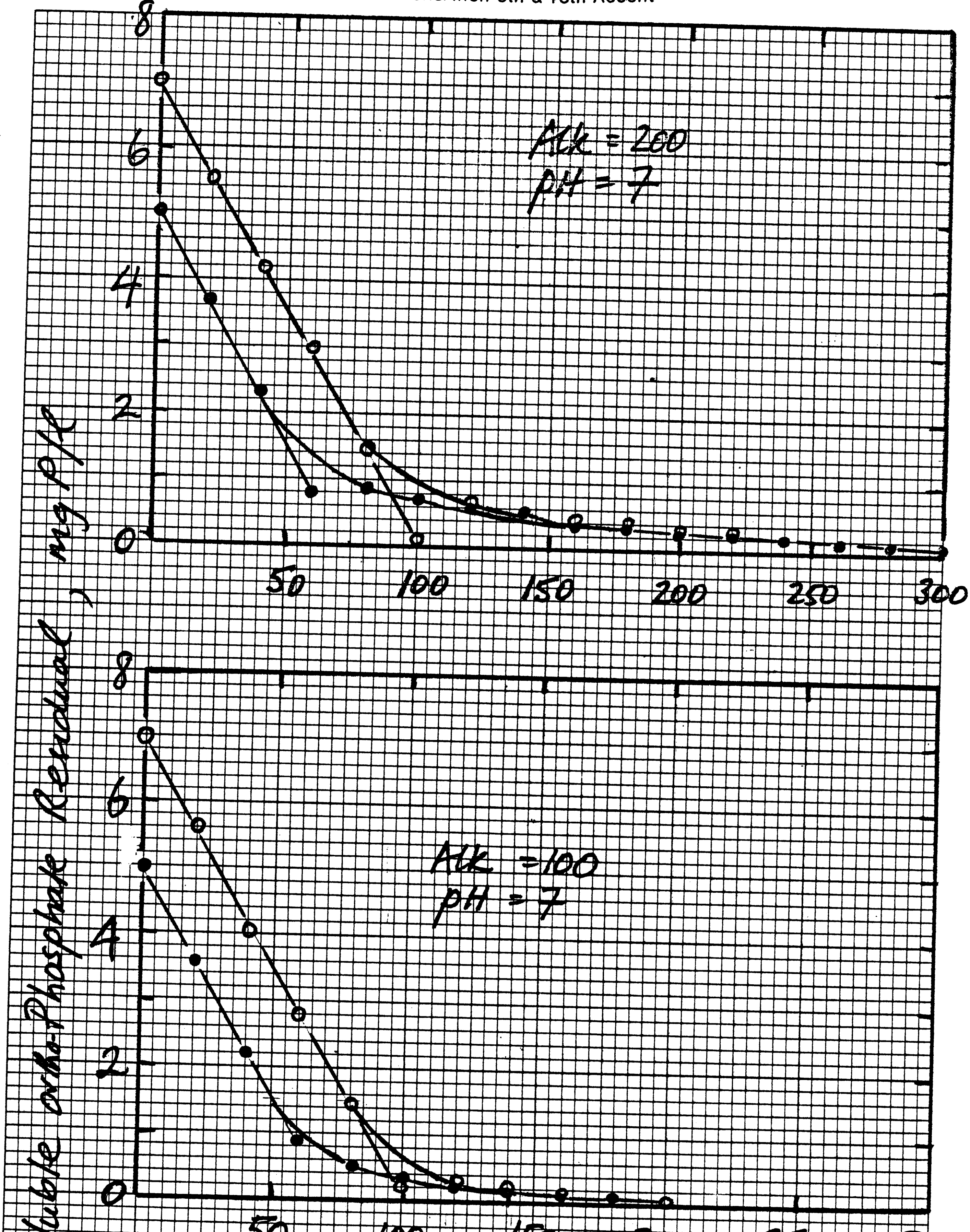
HELP

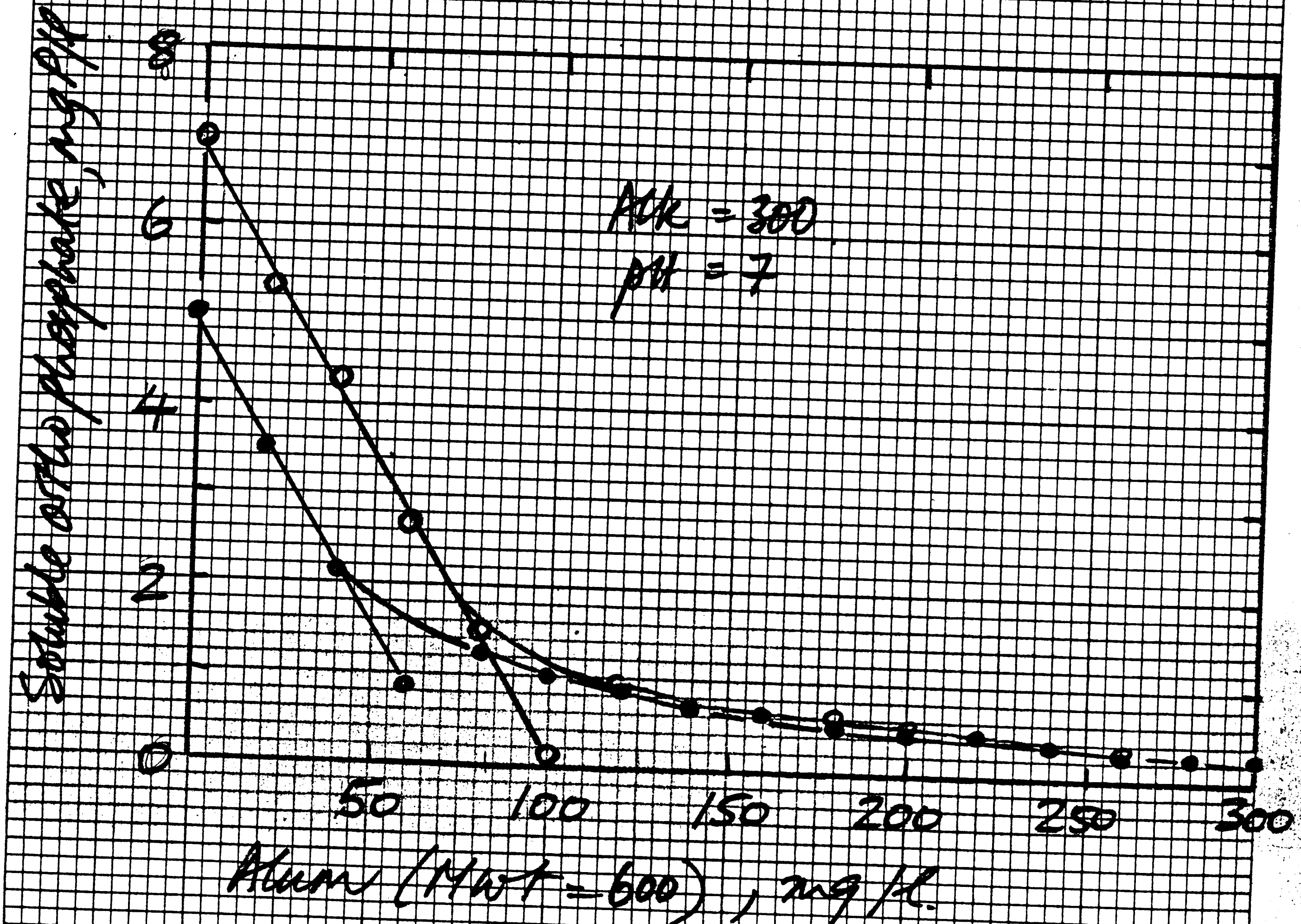
If you need further assistance in running the program contact:

Beverly James
James Engineering Inc.
6329 Fairmount Ave.
El Cerrito, CA 94530
(415)525-7350.

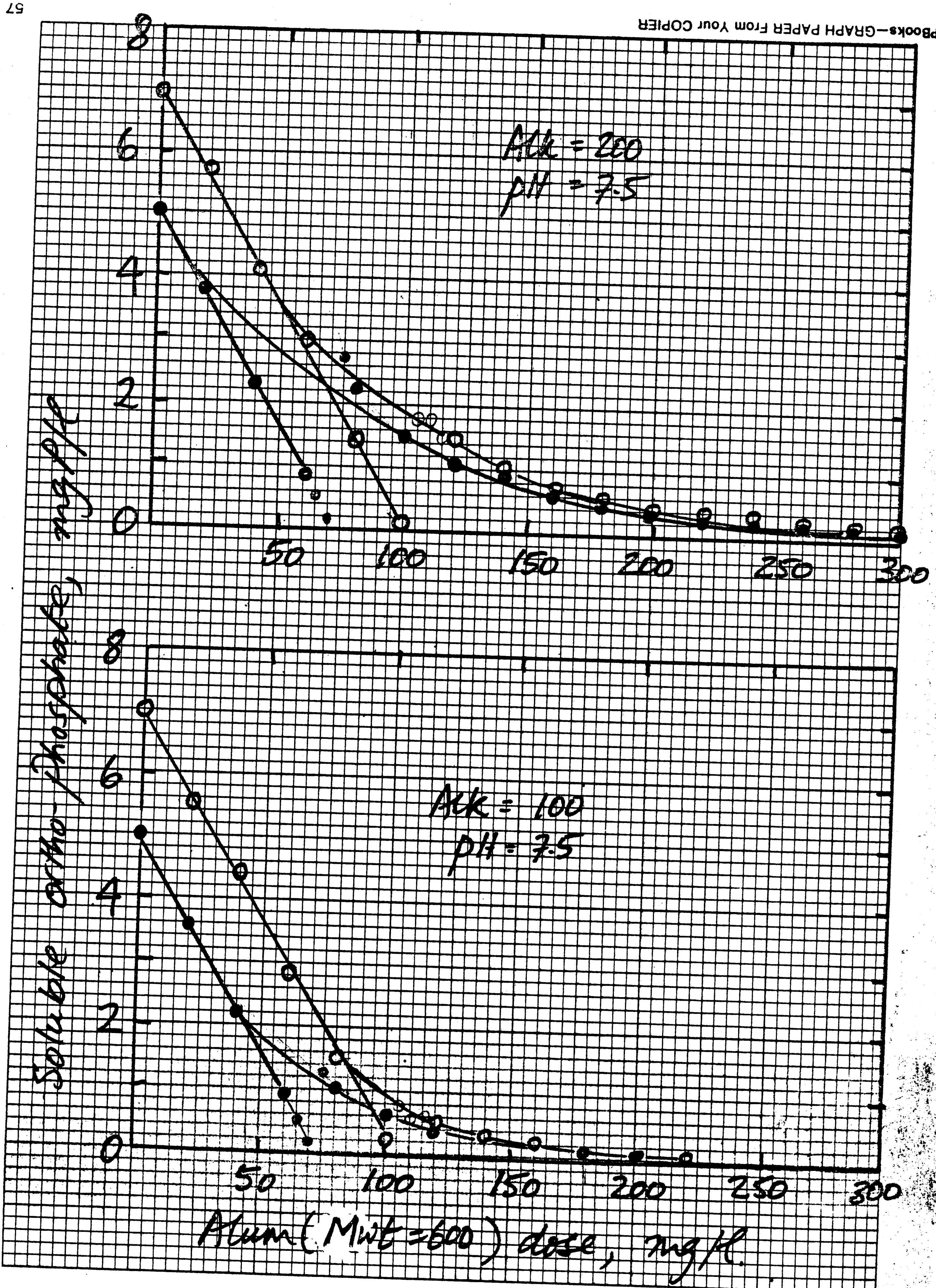
APPENDIX III

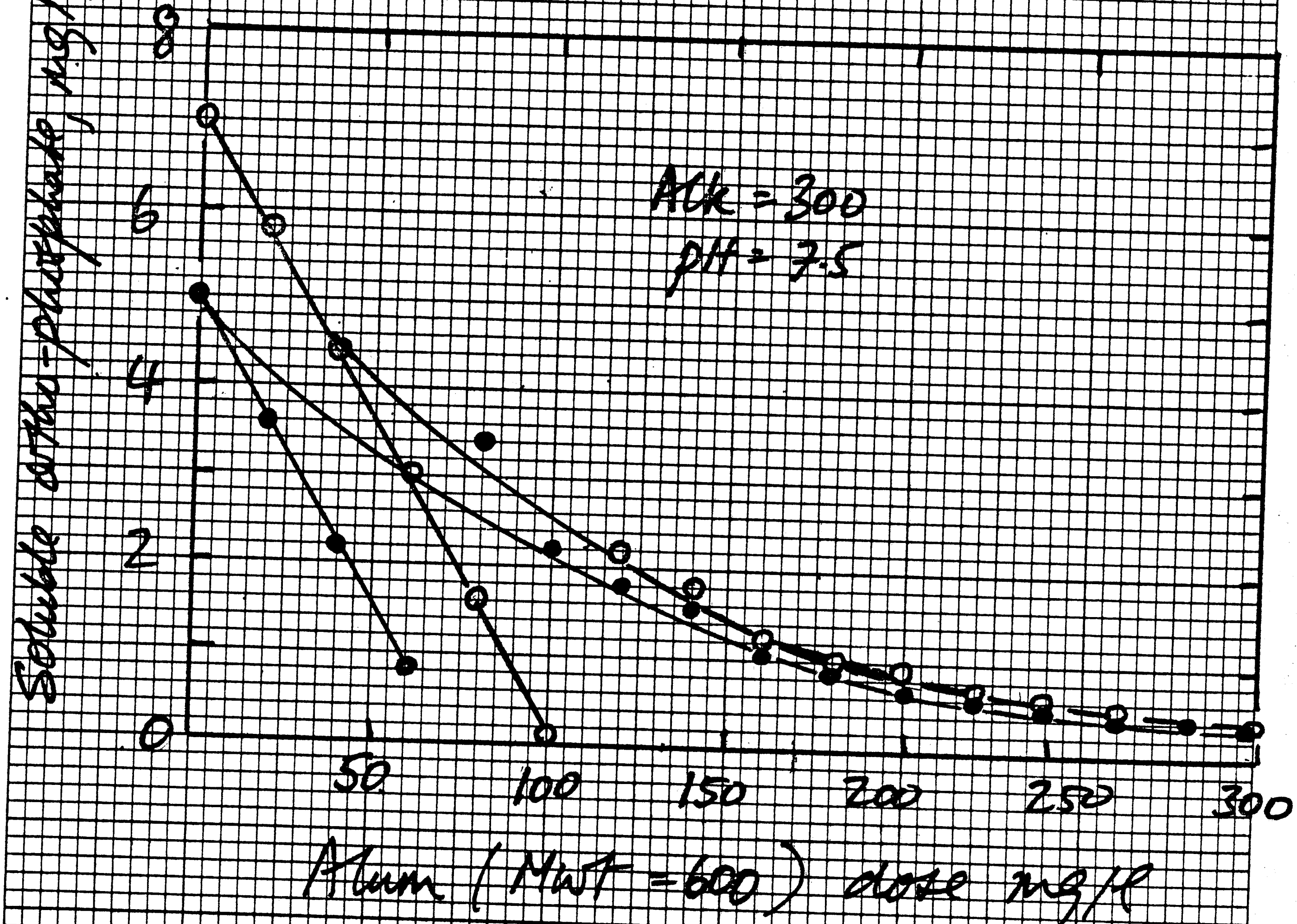
PHOSPHATE RESIDUAL/CHEMICAL DOSE FOR ALL CASES TESTED

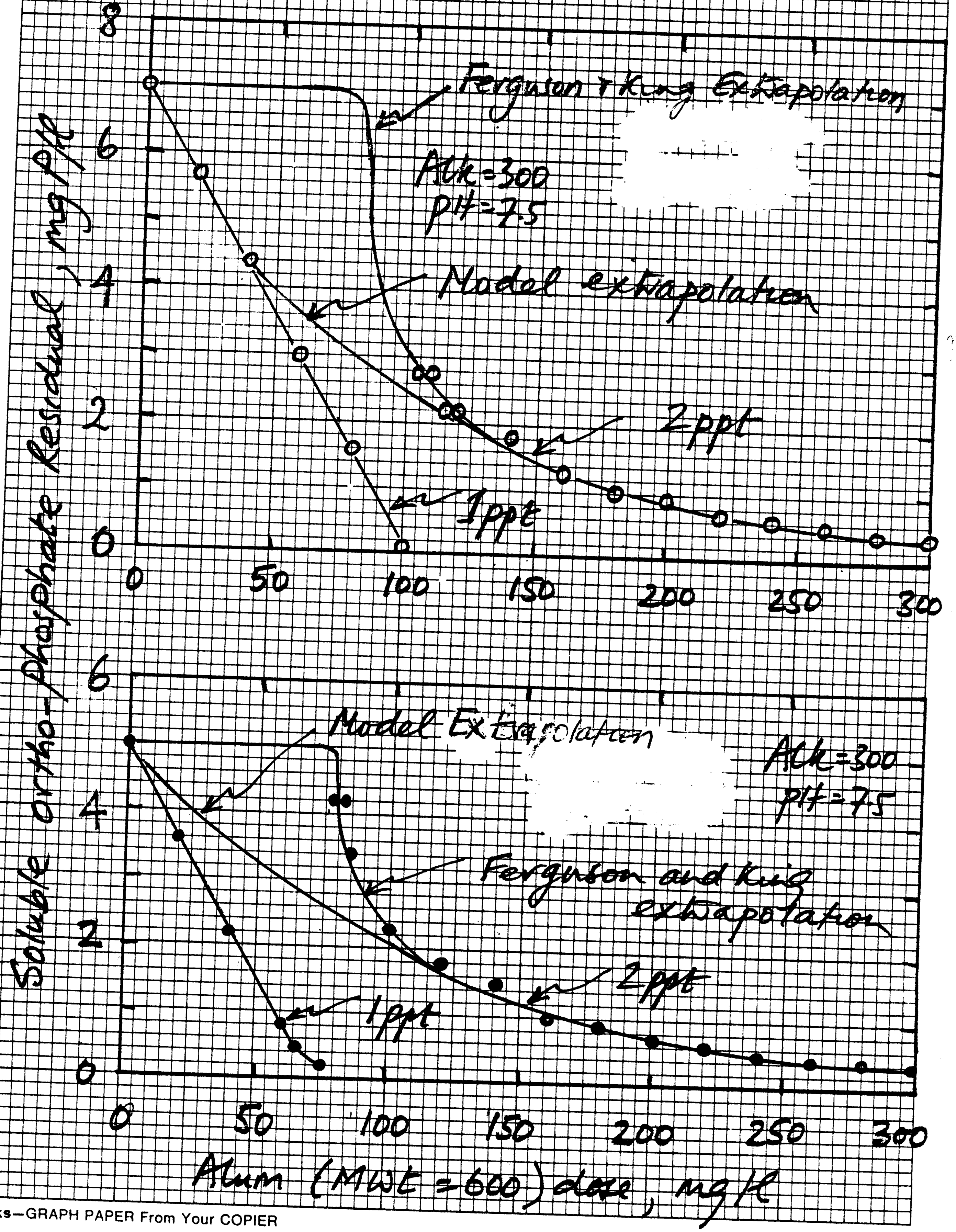

8
6
4
2
0
Alk = 200
pH = 7
50
100
150
200
250
300
8
6
4
2
0
Alk = 100
pH = 7
50
100
150
200
250
300
Soluble ortho-Phosphate Residual, mg P/l
Alum (Mwt = 600) dose, mg/l

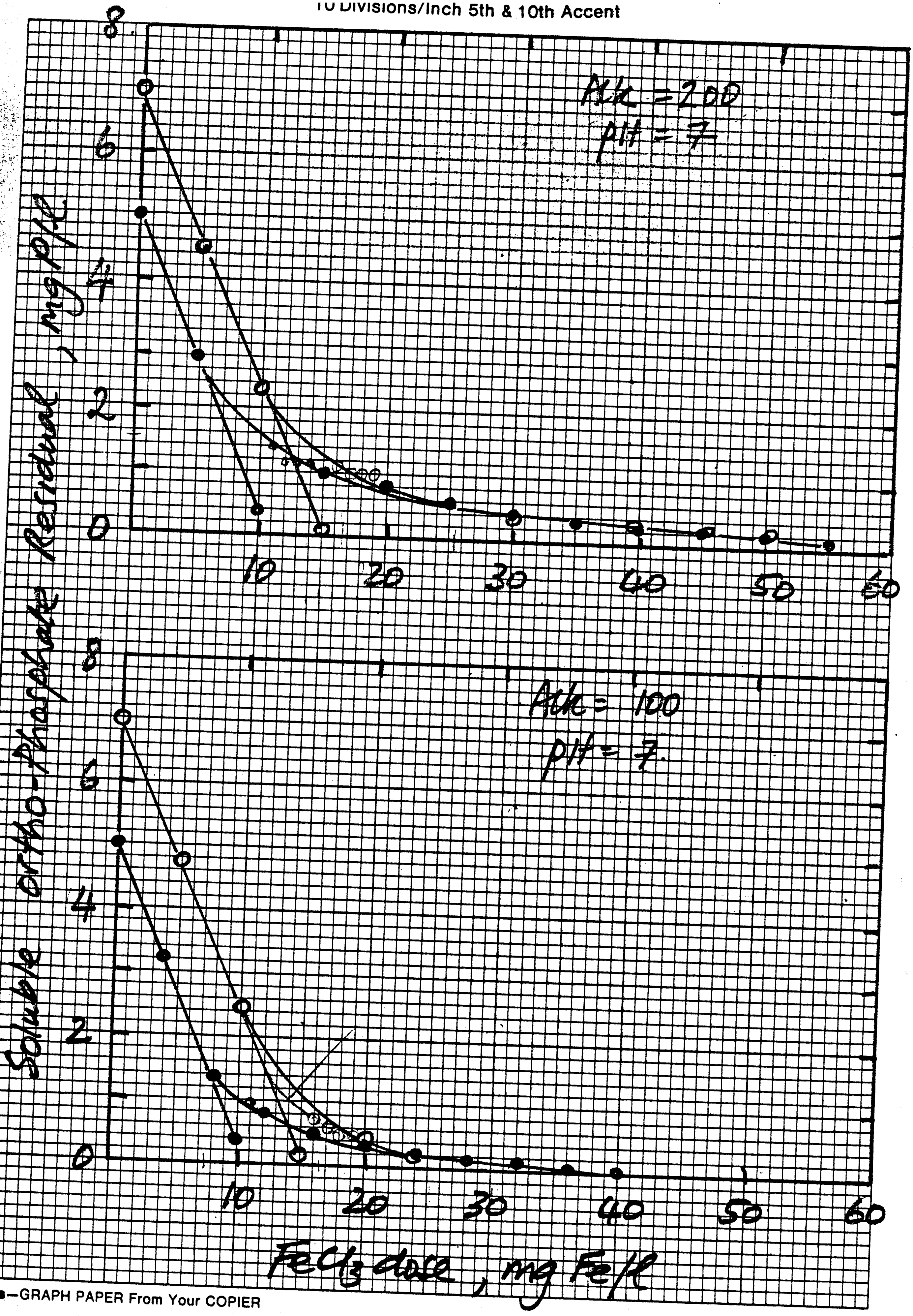

Soluble ortho phosphate, mg P/l
8
6
4
2
0
50
100
150
200
250
300
Alum (MWt = 600), mg/l
Alk = 300
pH = 7

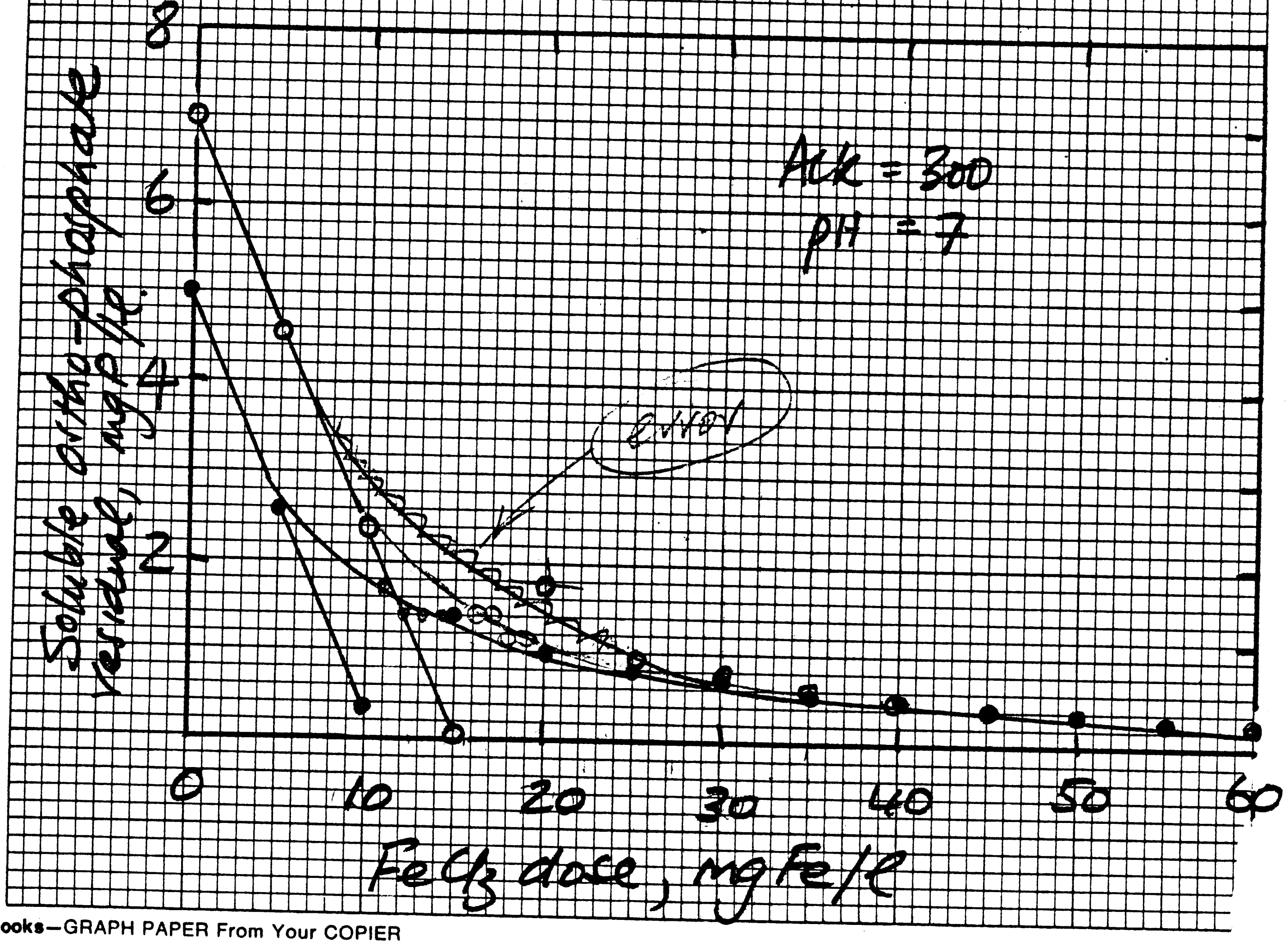
III-2.

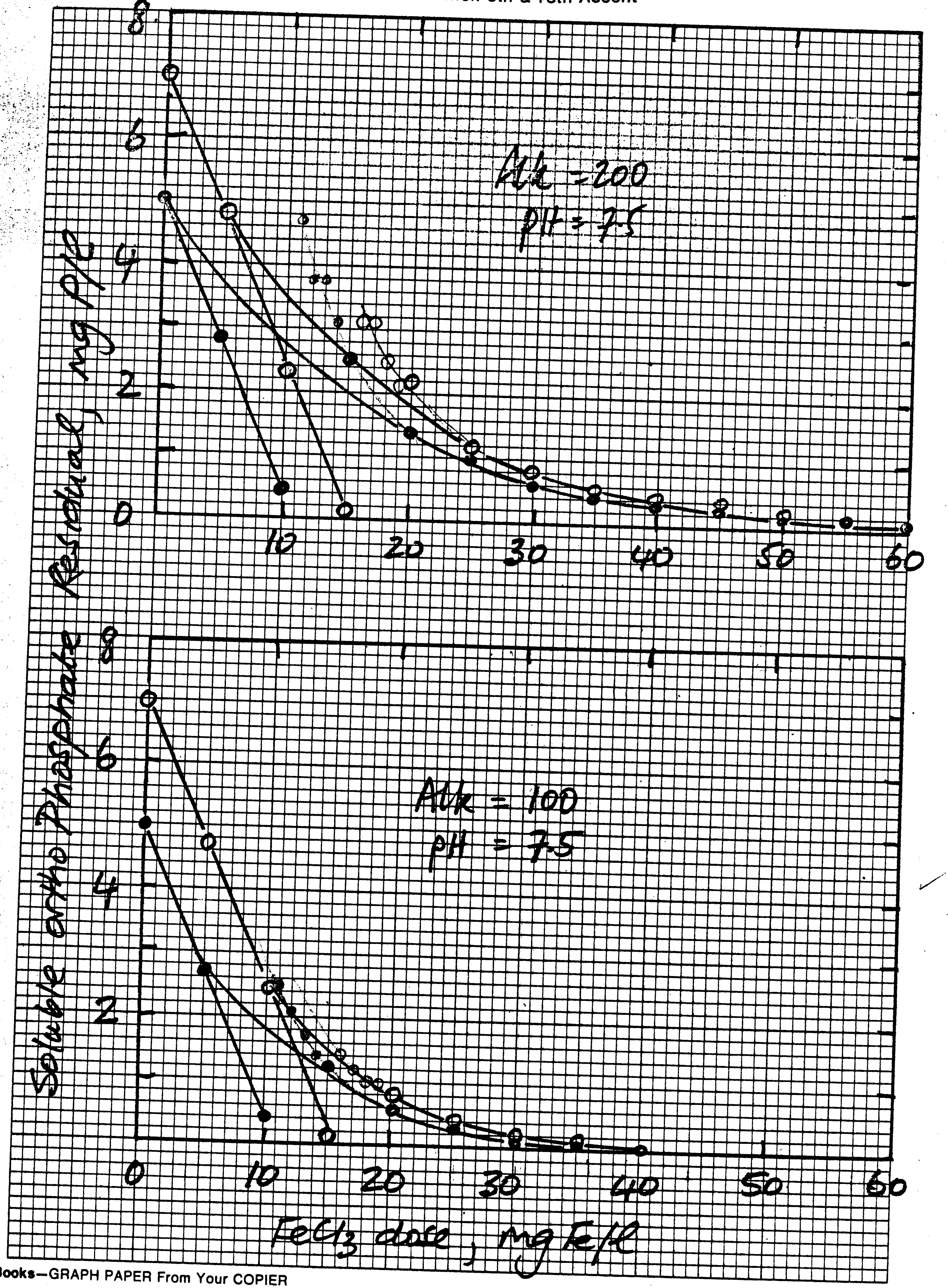

8
6
4
2
0
Alk = 200
pH = 7.5
50
100
150
200
250
300
8
6
4
2
0
Alk = 100
pH = 7.5
50
100
150
200
250
300
Soluble ortho-phosphate, mg P/l
Alum (Mwt = 600) dose, mg/l.

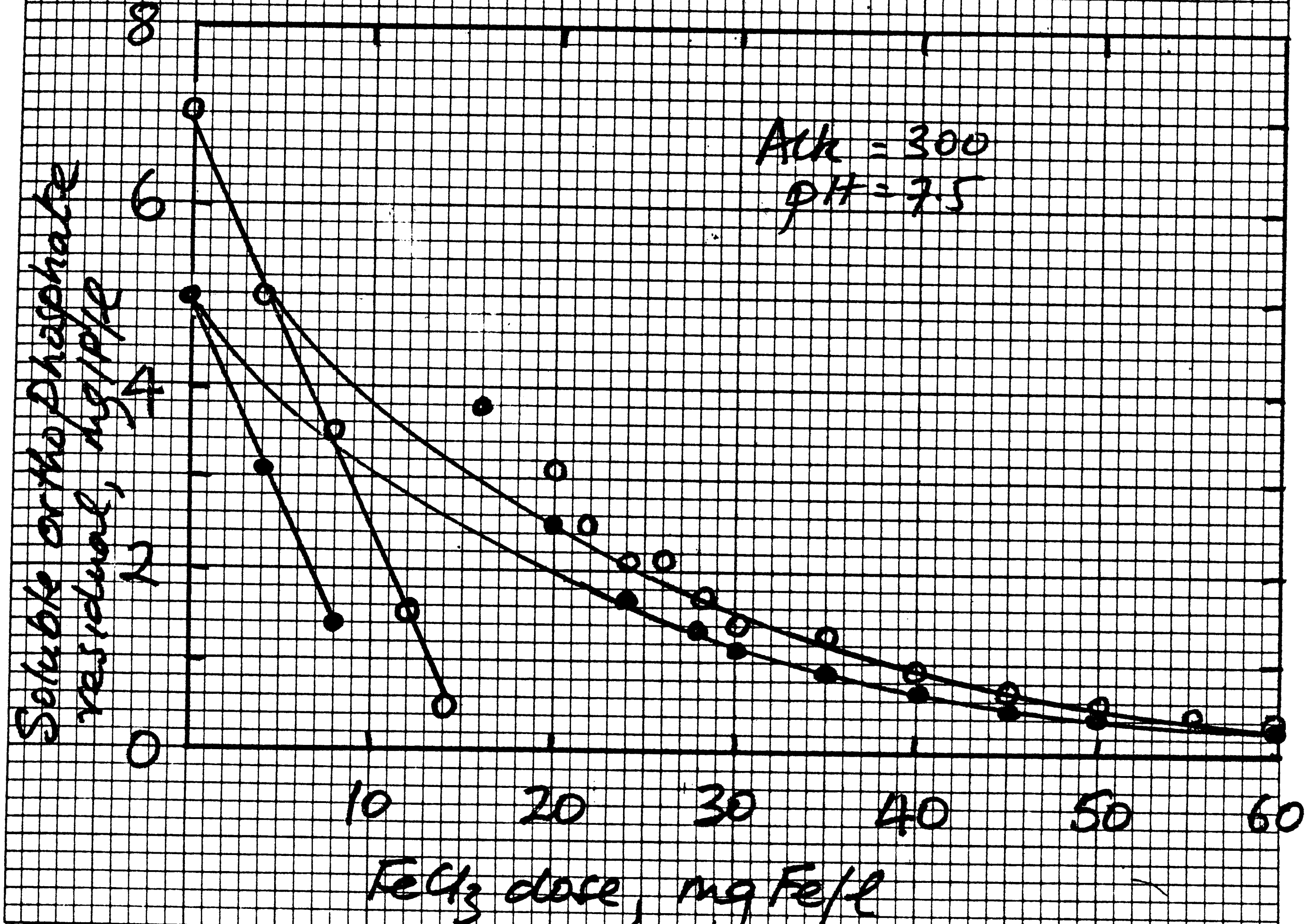

Soluble ortho-phosphate, mg P/l
8
6
4
2
0
Alk = 300
pH = 7.5
50
100
150
200
250
300
Alum (MWt = 600) dose mg/l

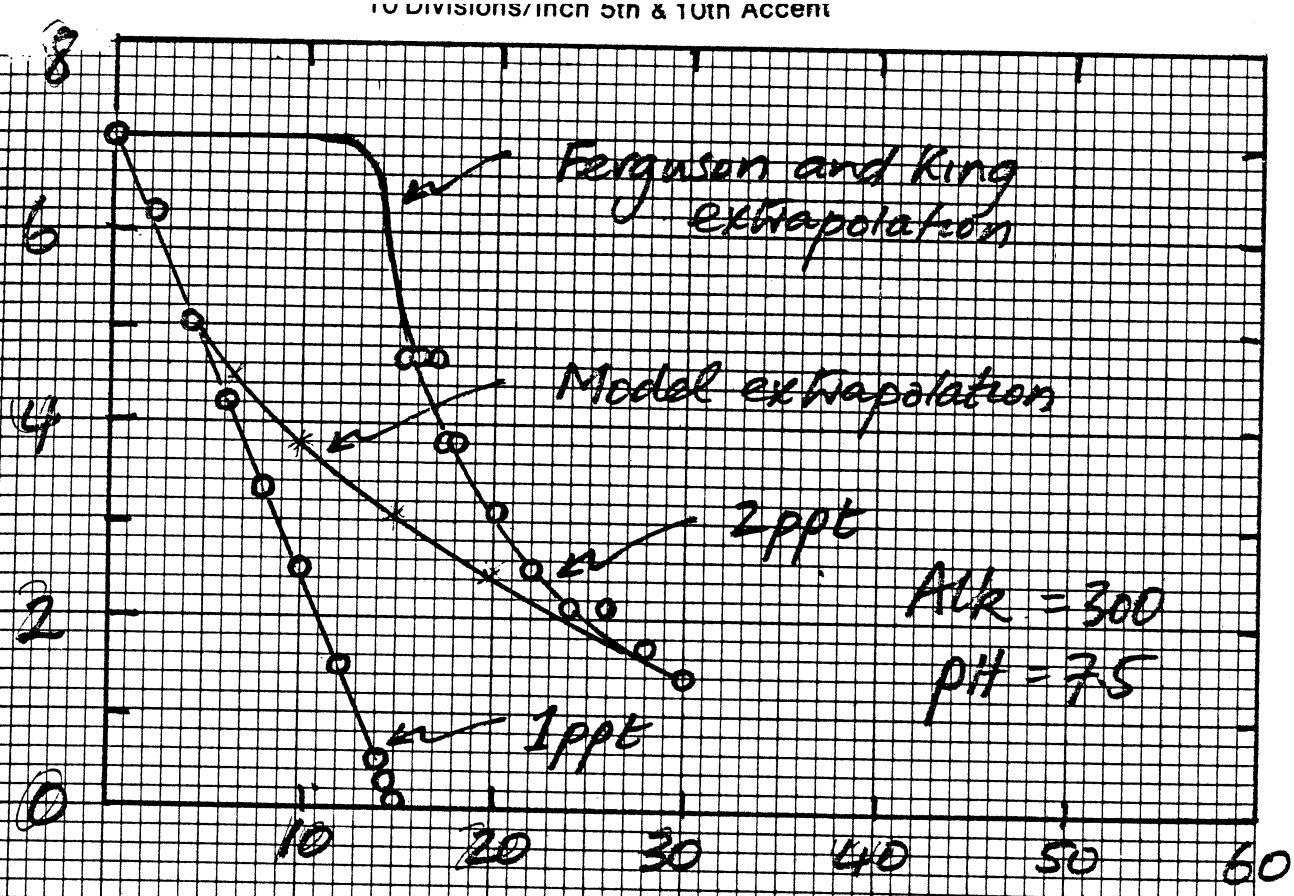

8
6
4
2
0
Ferguson + King Extrapolation
Alk=300
pH=7.5
Model extrapolation
2ppt
1ppt
0
50
100
150
200
250
300
6
4
2
0
Model Extrapolation
Alk=300
pH=7.5
Ferguson and King extrapolation
2ppt
1ppt
0
50
100
150
200
250
300
Soluble ortho-Phosphate Residual, mg P/l
Alum (MWt = 600) dose, mg/l

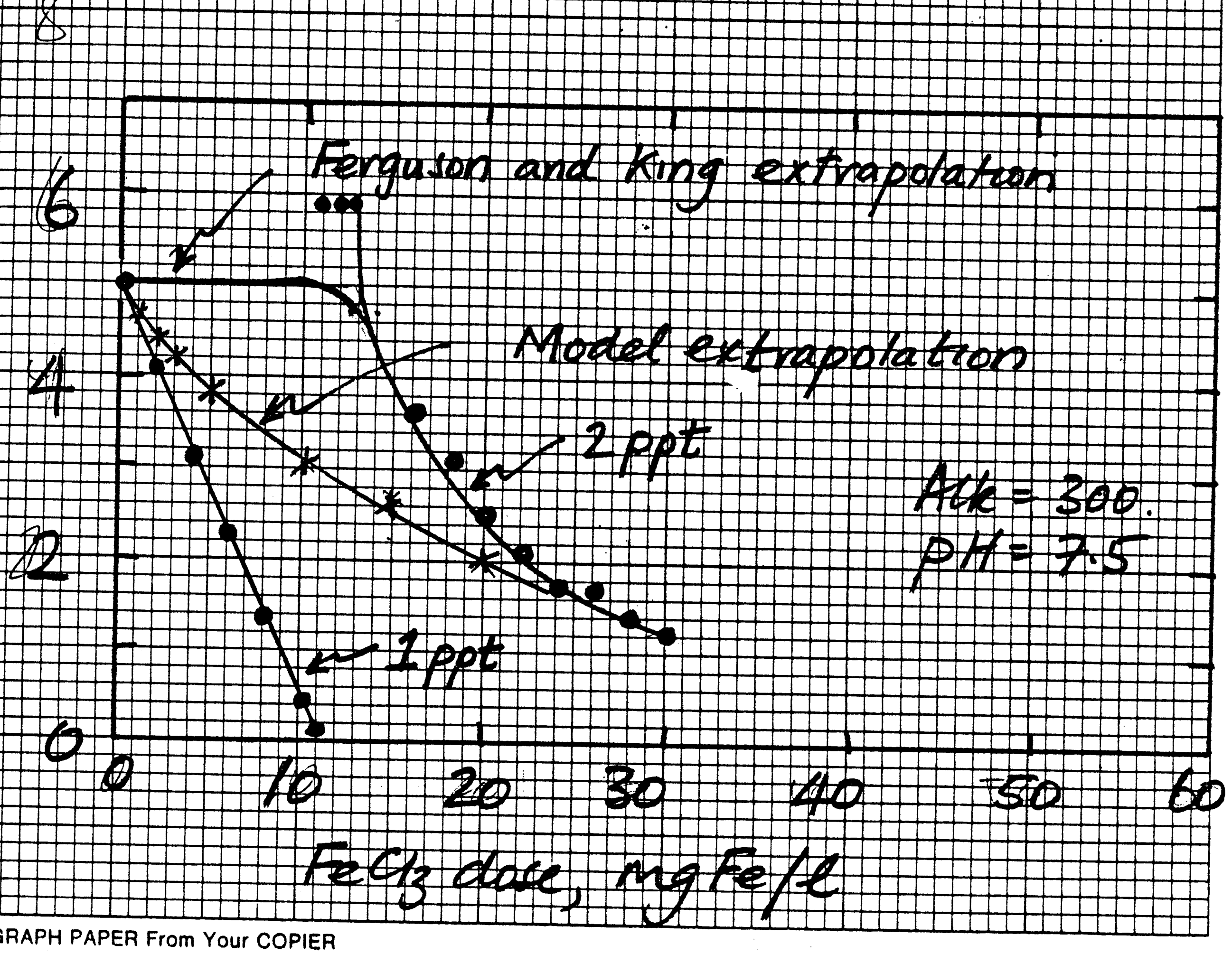

8
6
4
2
0
Alk = 200
pH = 7
10
20
30
40
50
60
Soluble ortho-Phosphate Residual, mg P/l
8
6
4
2
0
Alk = 100
pH = 7
10
20
30
40
50
60
FeCl$_3$ dose, mg Fe/l

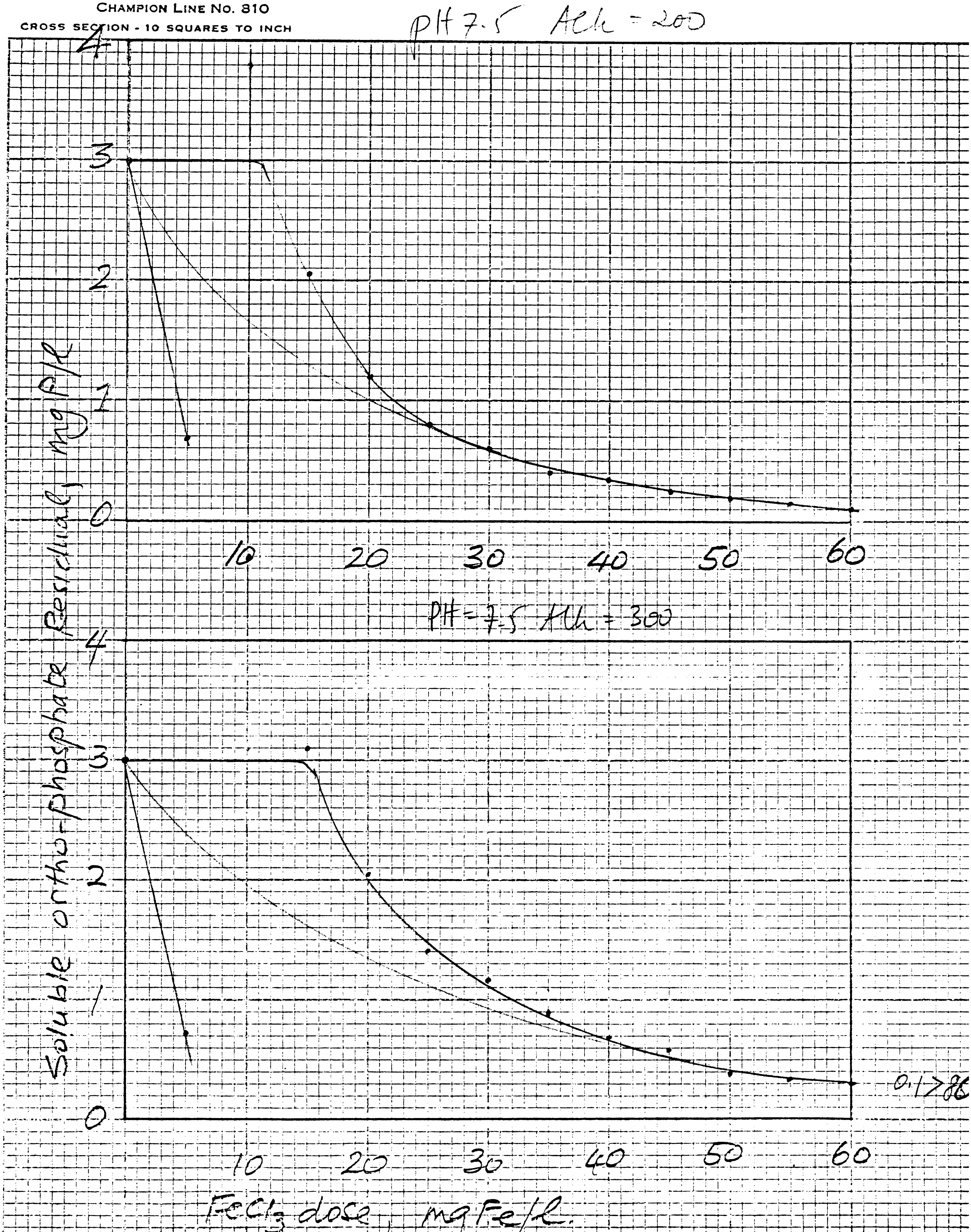

Soluble ortho-phosphate residual, mg P/l
8
6
4
2
0
10
20
30
40
50
60
FeCl3 dose, mg Fe/l
Alk = 300
pH = 7
error

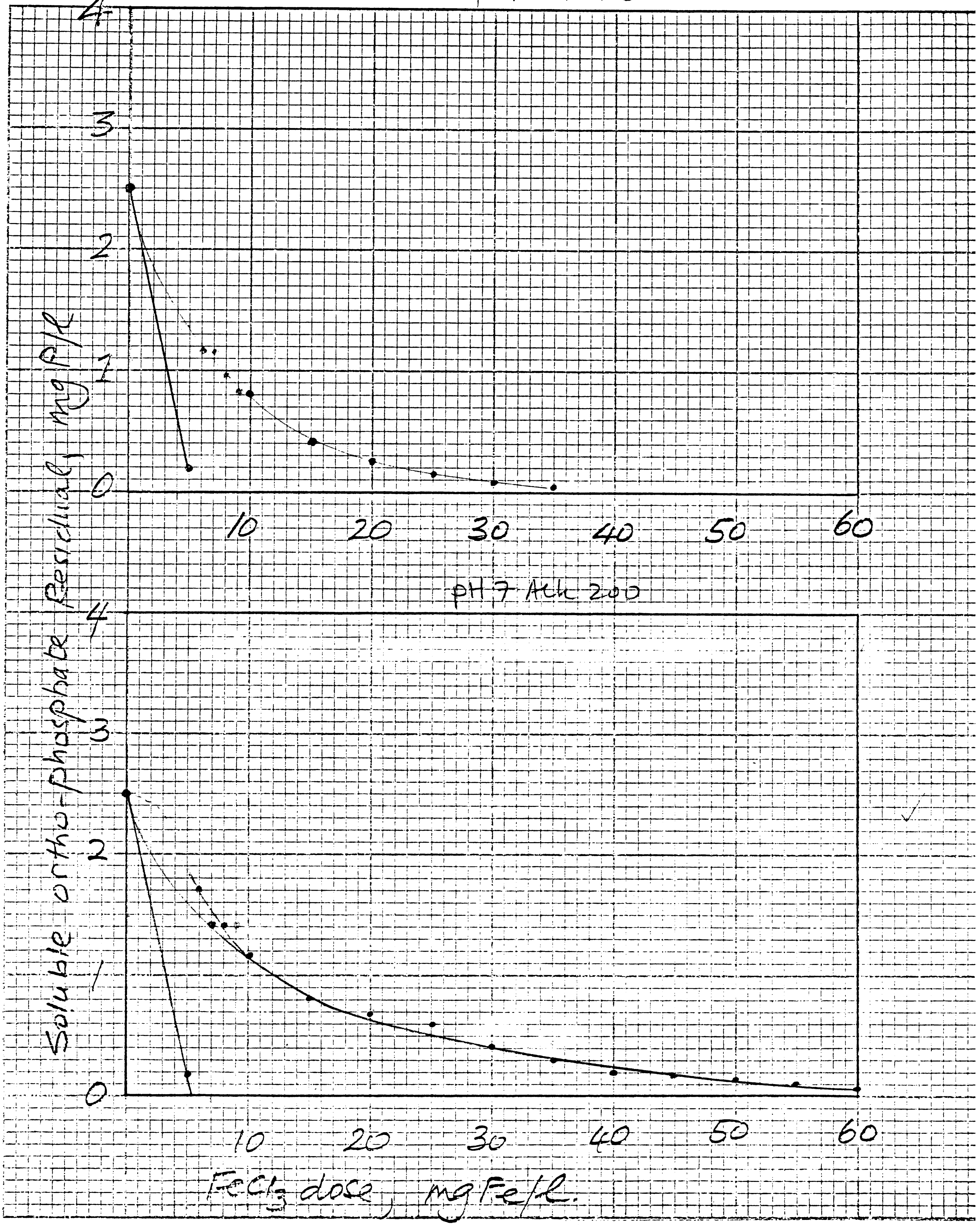

8
6
4
2
0
Alk = 200
pH = 7.5
10
20
30
40
50
60
8
6
4
2
Alk = 100
pH = 7.5
0
10
20
30
40
50
60
Soluble ortho Phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l

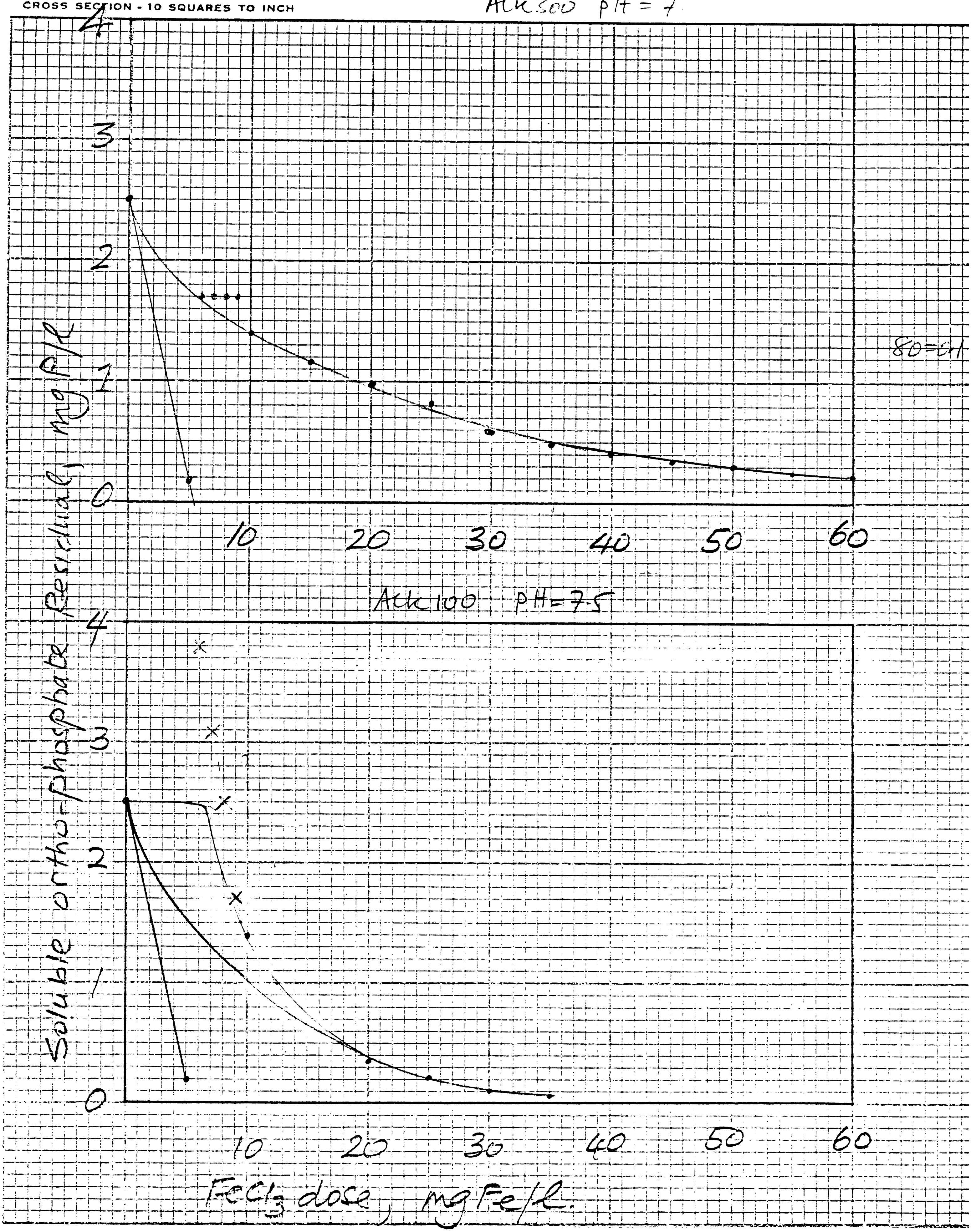

8
6
4
2
0
Soluble ortho phosphate residual, mg/P/l
Alk = 300
pH = 7.5
10
20
30
40
50
60
$FeCl_3$ dose, mg Fe/l

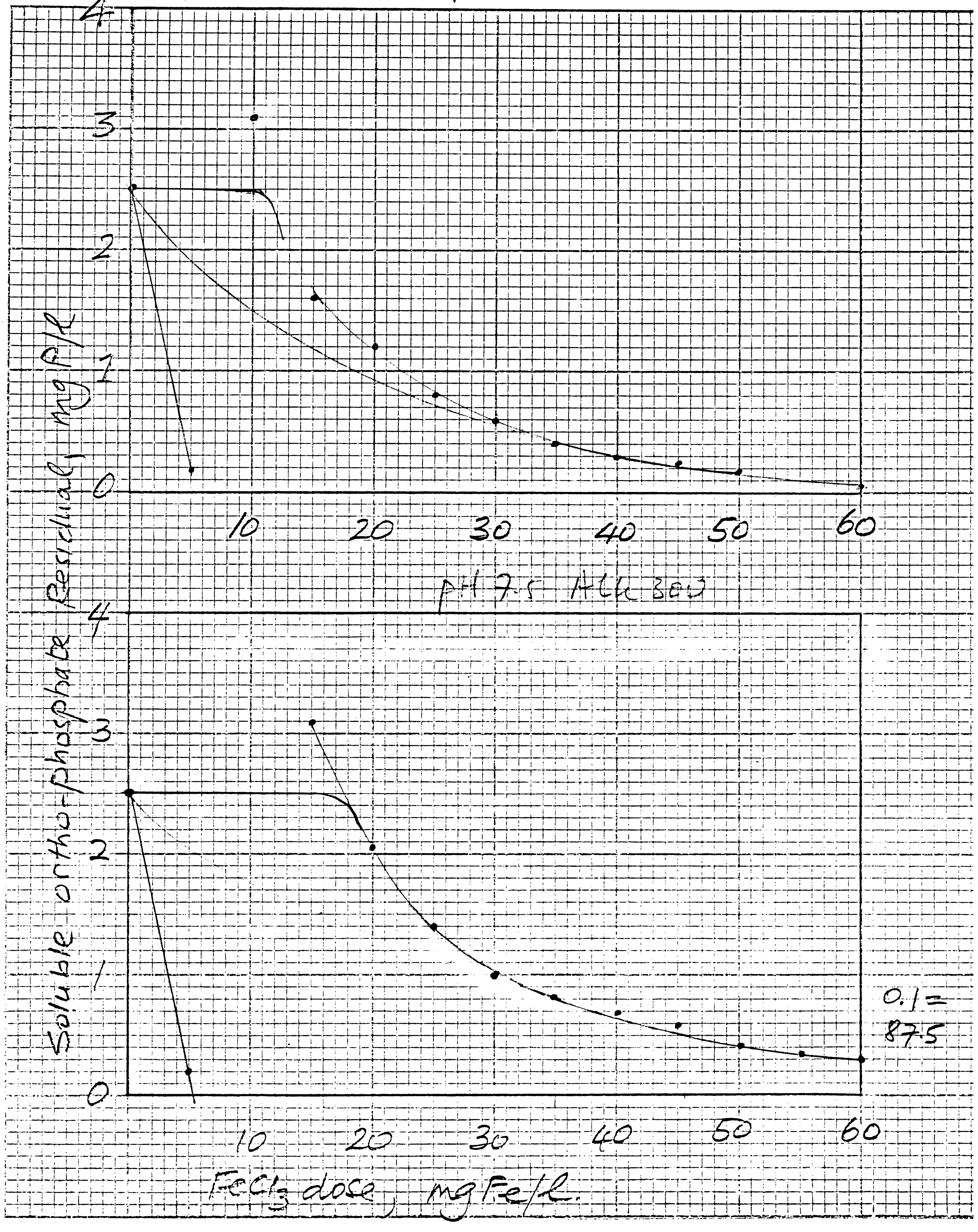

8
6
4
2
0
10
20
30
40
50
60
Ferguson and King extrapolation
Model extrapolation
2ppt
1ppt
Alk = 300
pH = 7.5


8
6
4
2
0
0
10
20
30
40
50
60
Ferguson and King extrapolation
Model extrapolation
2ppt
1ppt
Alk = 300.
PH = 7.5
FeCl3 dose, mg Fe/l


pH 7.5 Alk = 200
4
3
2
1
0
10
20
30
40
50
60
PH = 7.5 Alk = 300
4
3
2
1
0
0.1>86
10
20
30
40
50
60
Soluble ortho-phosphate Residual, mg P/l
FeCl$_3$ dose, mg Fe/l.

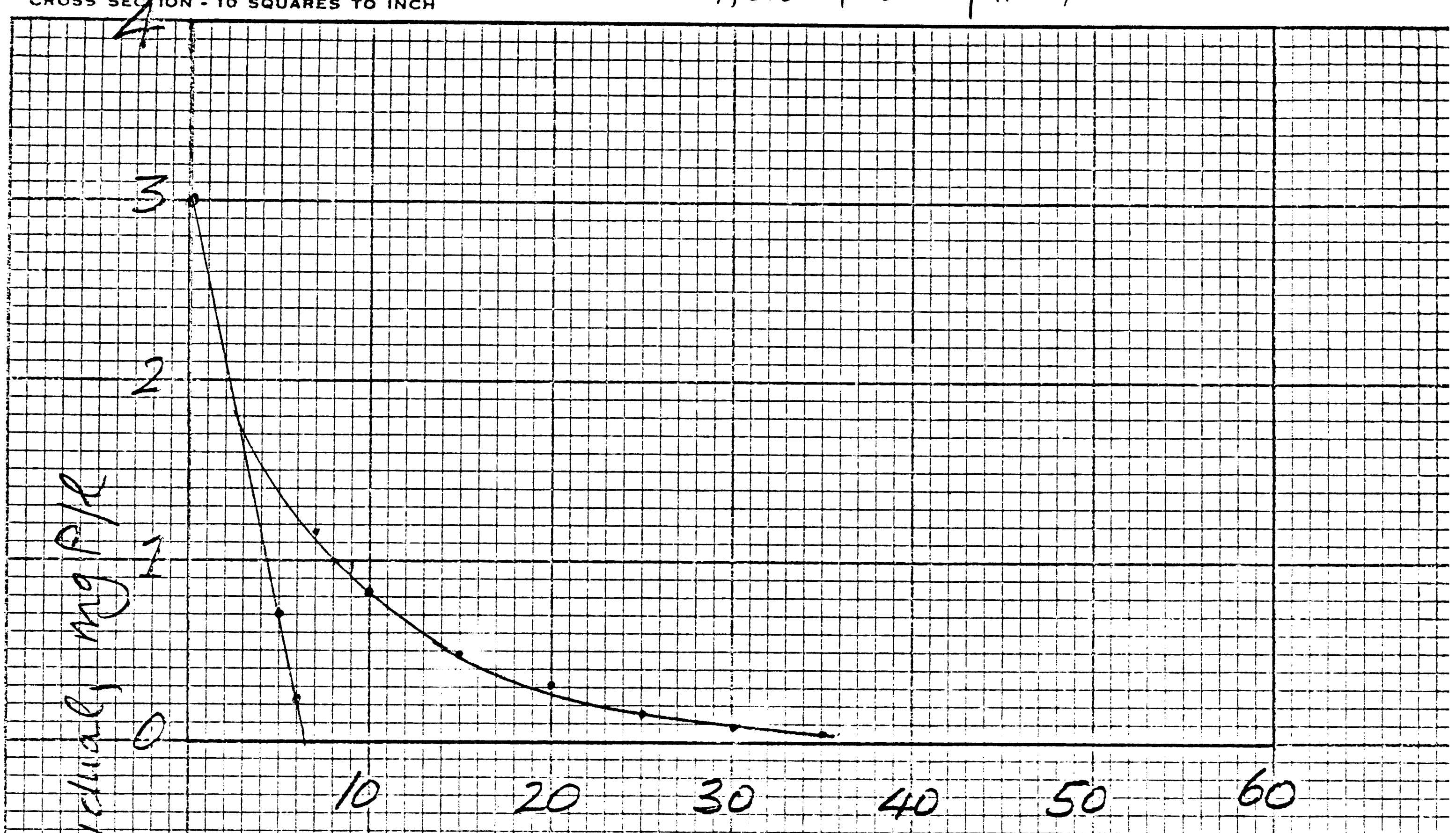

pH7 Alk 100
4
3
2
1
0
10
20
30
40
50
60
pH 7 Alk 200
4
3
2
1
0
10
20
30
40
50
60
Soluble ortho-phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l.


Alk300 pH = 7
4
3
2
1
0
10
20
30
40
50
60
80=0.1
Alk100 pH=7.5
4
3
2
1
0
10
20
30
40
50
60
Soluble ortho-phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l.

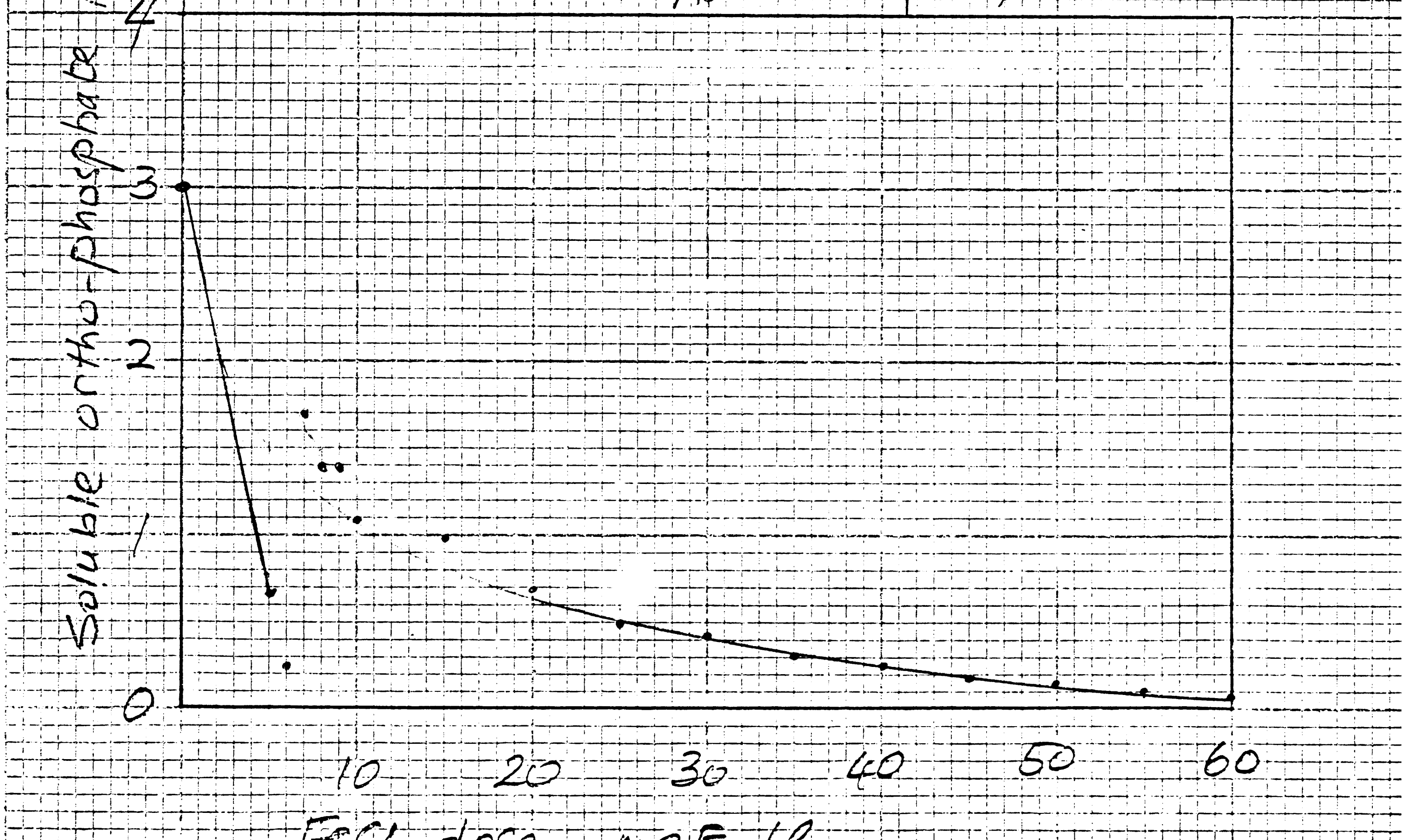

pH = 7.5 Alk = 200
4
3
2
1
0
10
20
30
40
50
60
pH 7.5 Alk 300
4
3
2
1
0
10
20
30
40
50
60
0.1 =
87.5
Soluble ortho-phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l.

CHAMPION LINE NO. 810
CROSS SECTION - 10 SQUARES TO INCH

Alk = 100 pH = 7

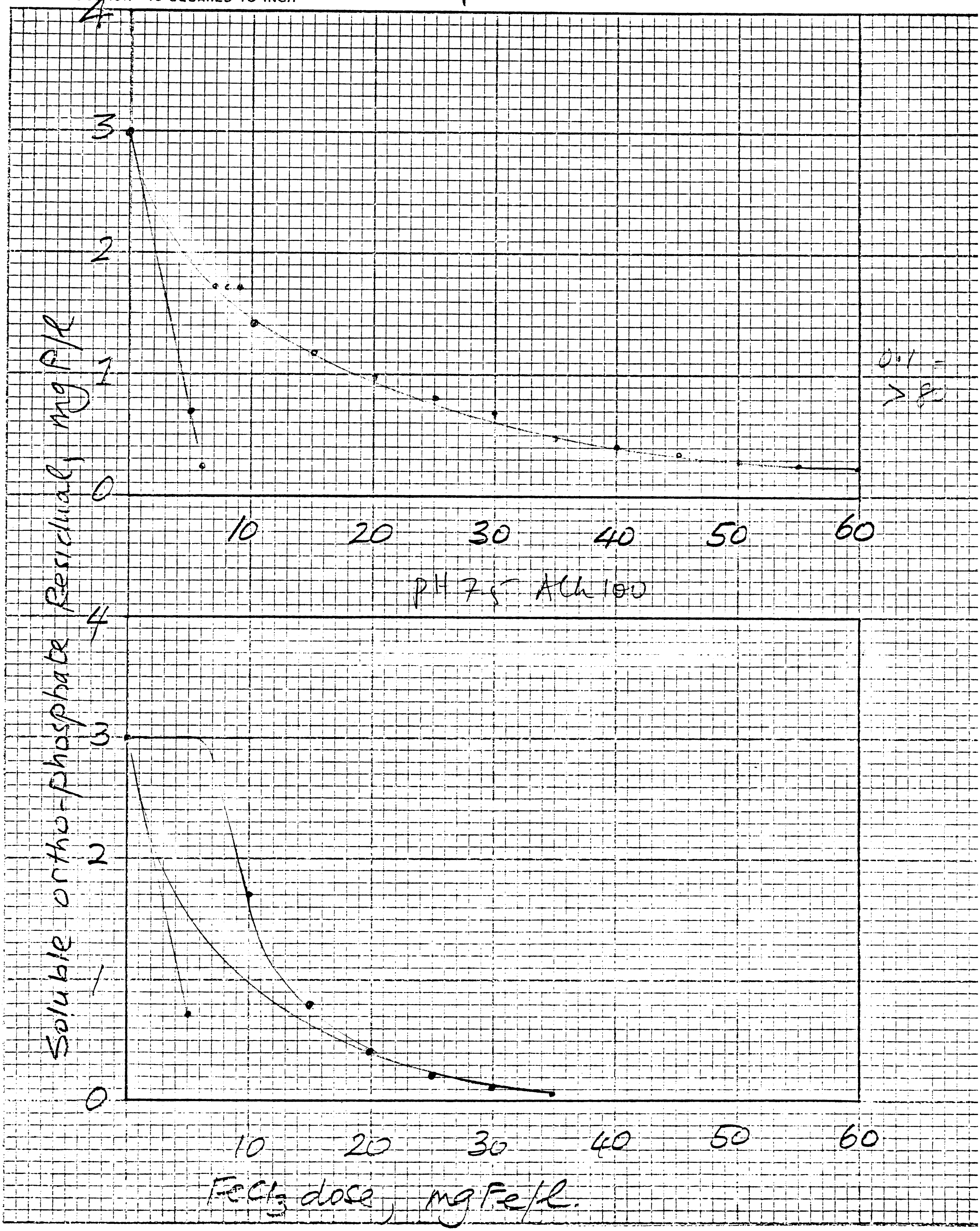


Alk 200 pH = 7

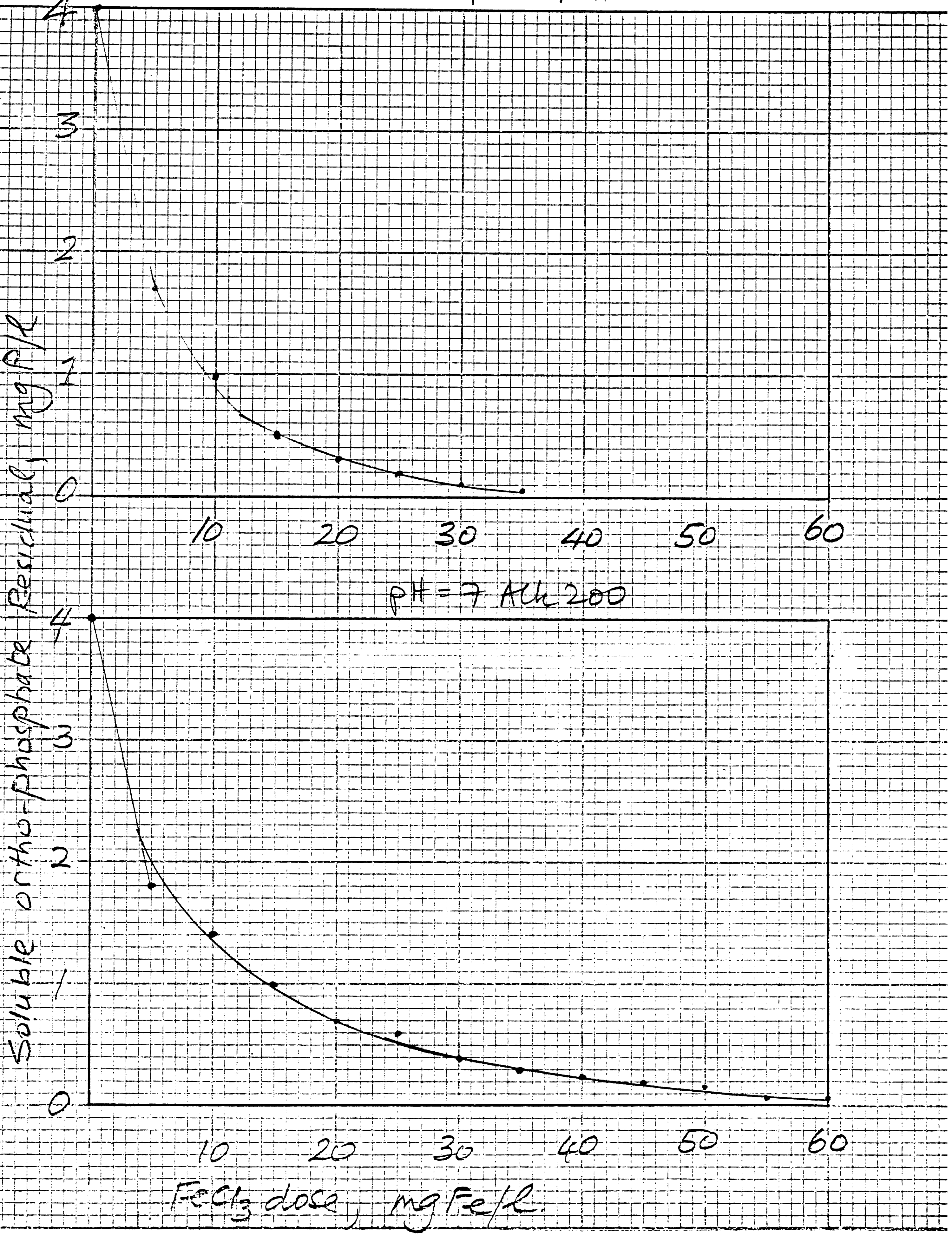


CHAMPION LINE NO. 810
CROSS SECTION - 10 SQUARES TO INCH

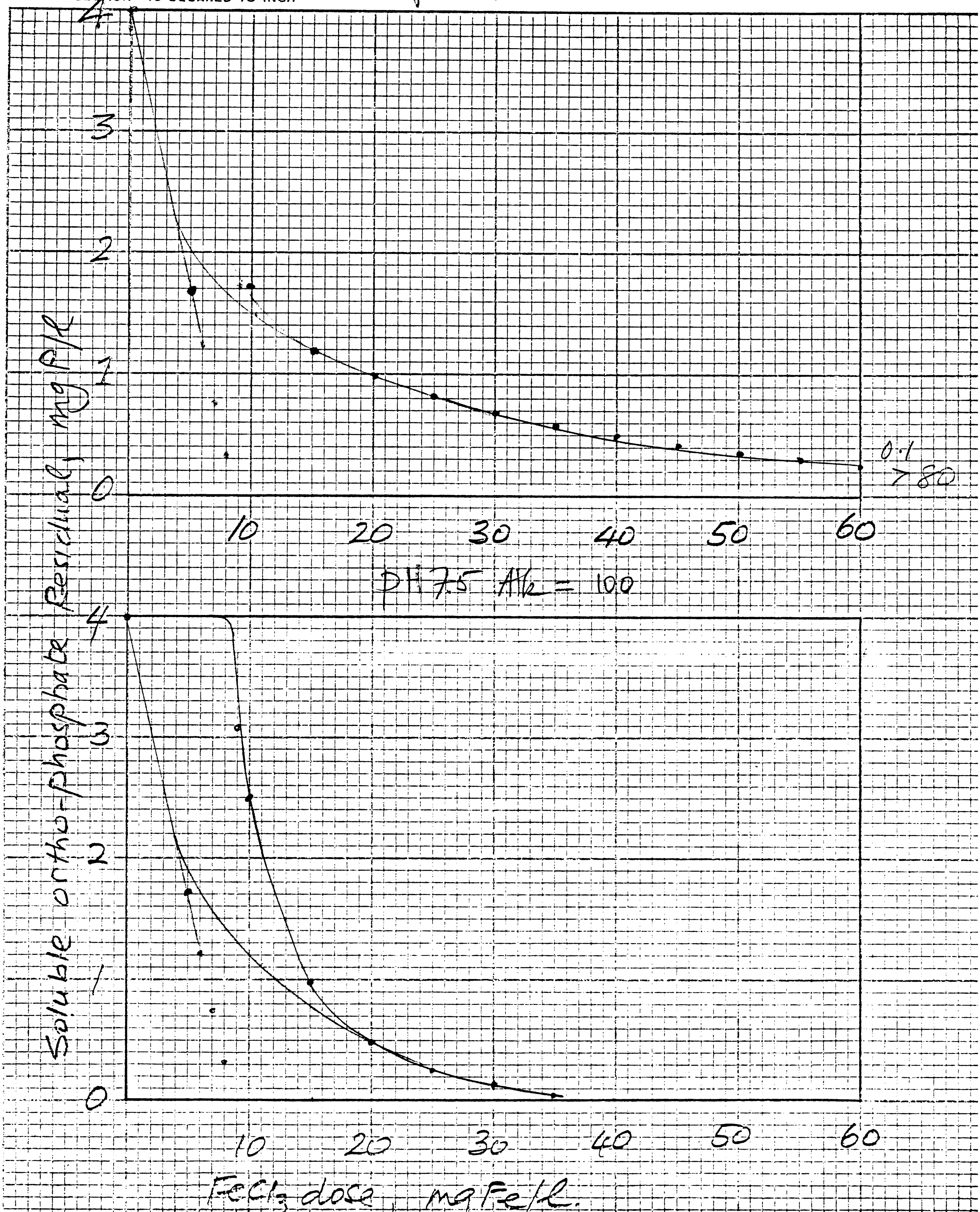
pH 7 Alk 300



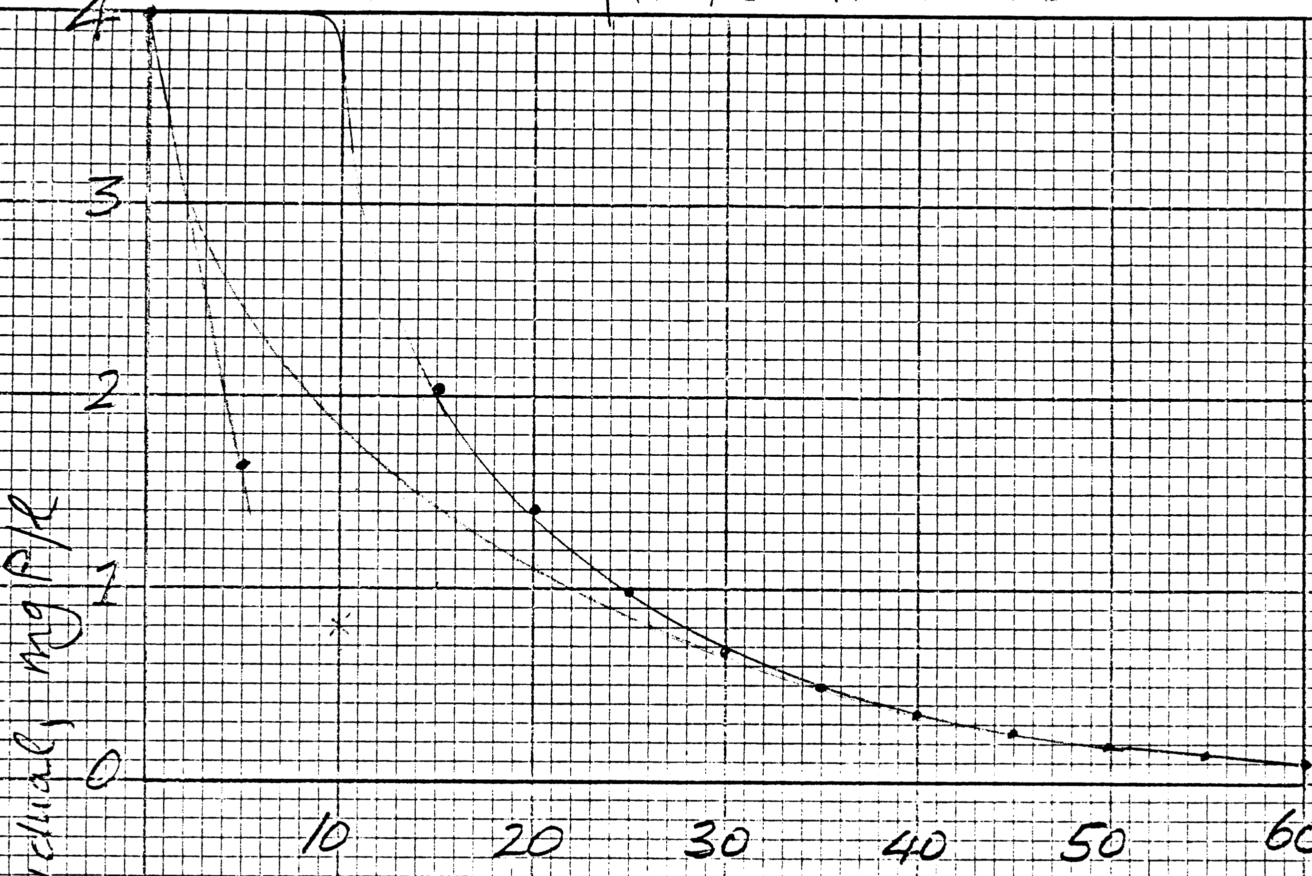
pH = 7 Alk 100


4
3
2
1
0
10
20
30
40
50
60
pH = 7 Alk 200
4
3
2
1
0
10
20
30
40
50
60
Soluble ortho-phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l.

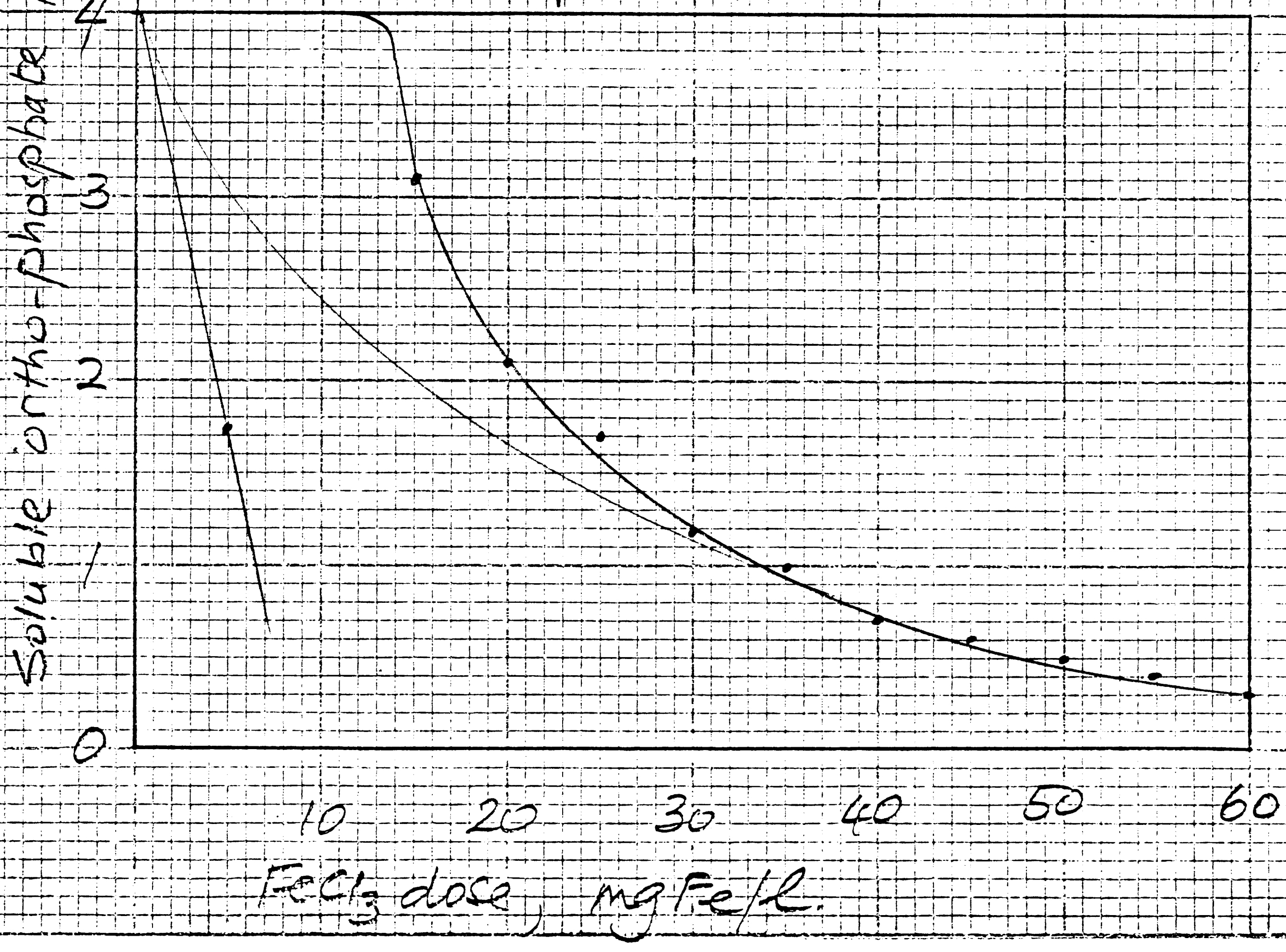
pH = 7 Alk = 300


4
3
2
1
0
0.1
>80
10
20
30
40
50
60
PH 7.5 Alk = 100
4
3
2
1
0
10
20
30
40
50
60
Soluble ortho-phosphate Residual, mg P/l
FeCl3 dose, mg Fe/l.

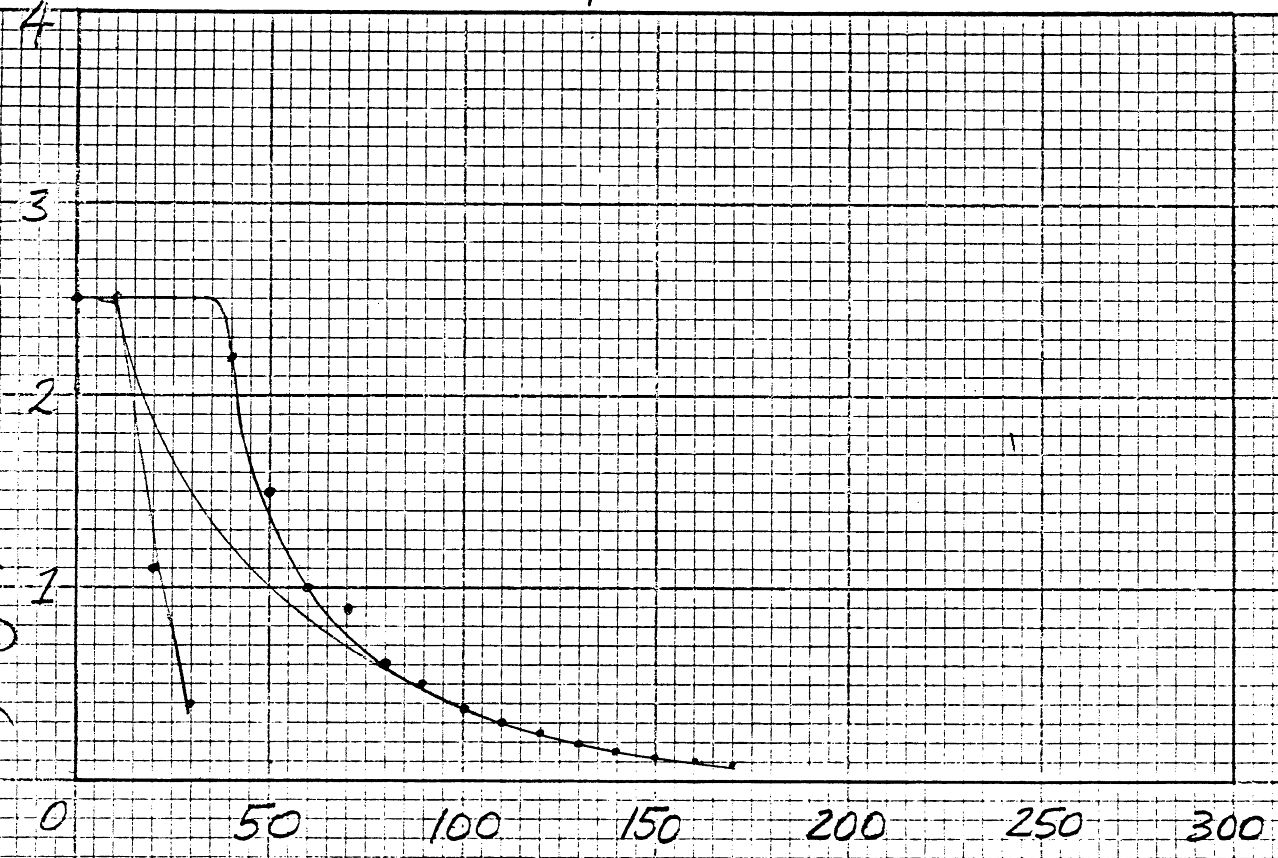
pH 7.5 Alk = 200



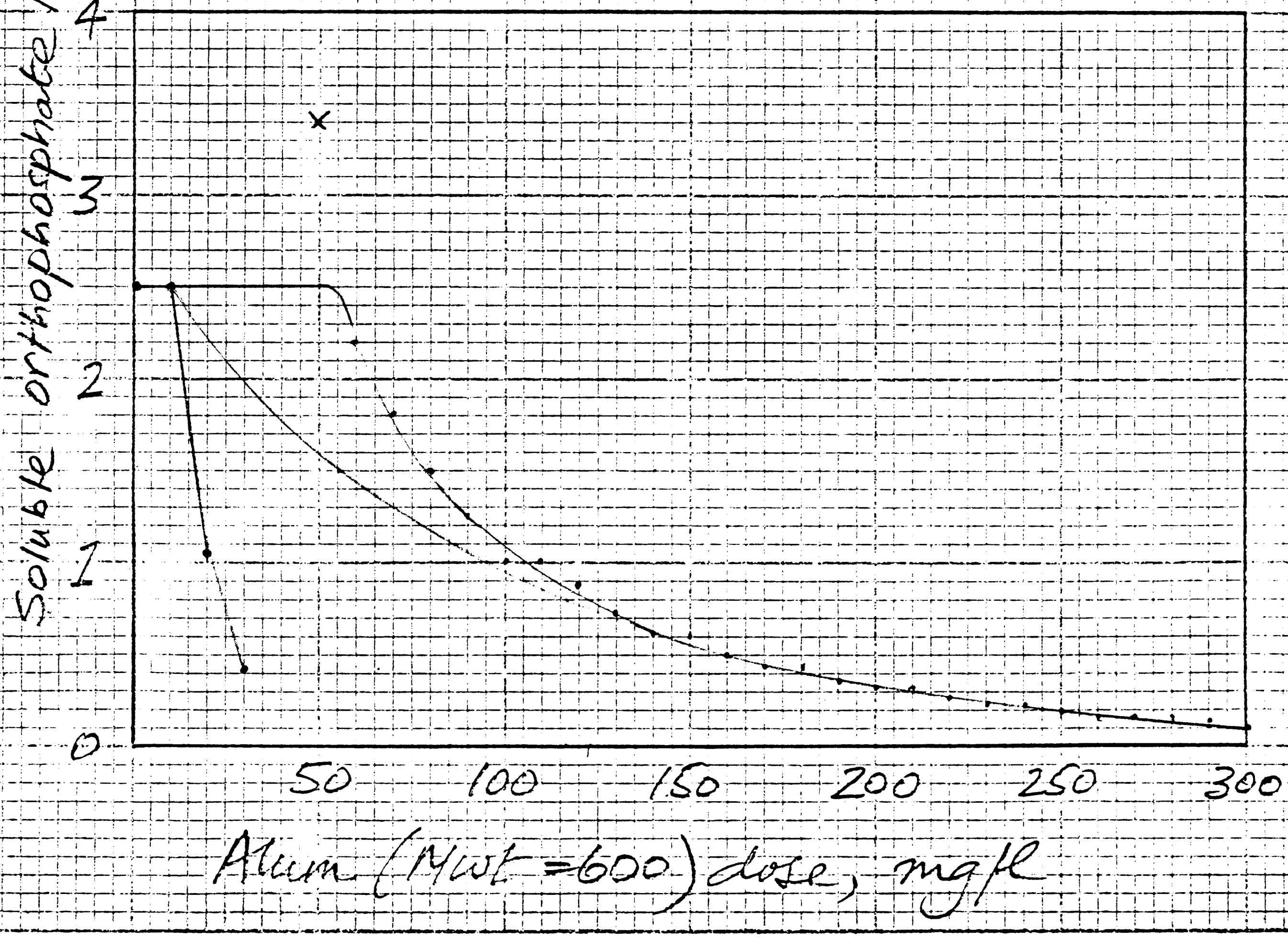
pH 7.5 Alk = 300

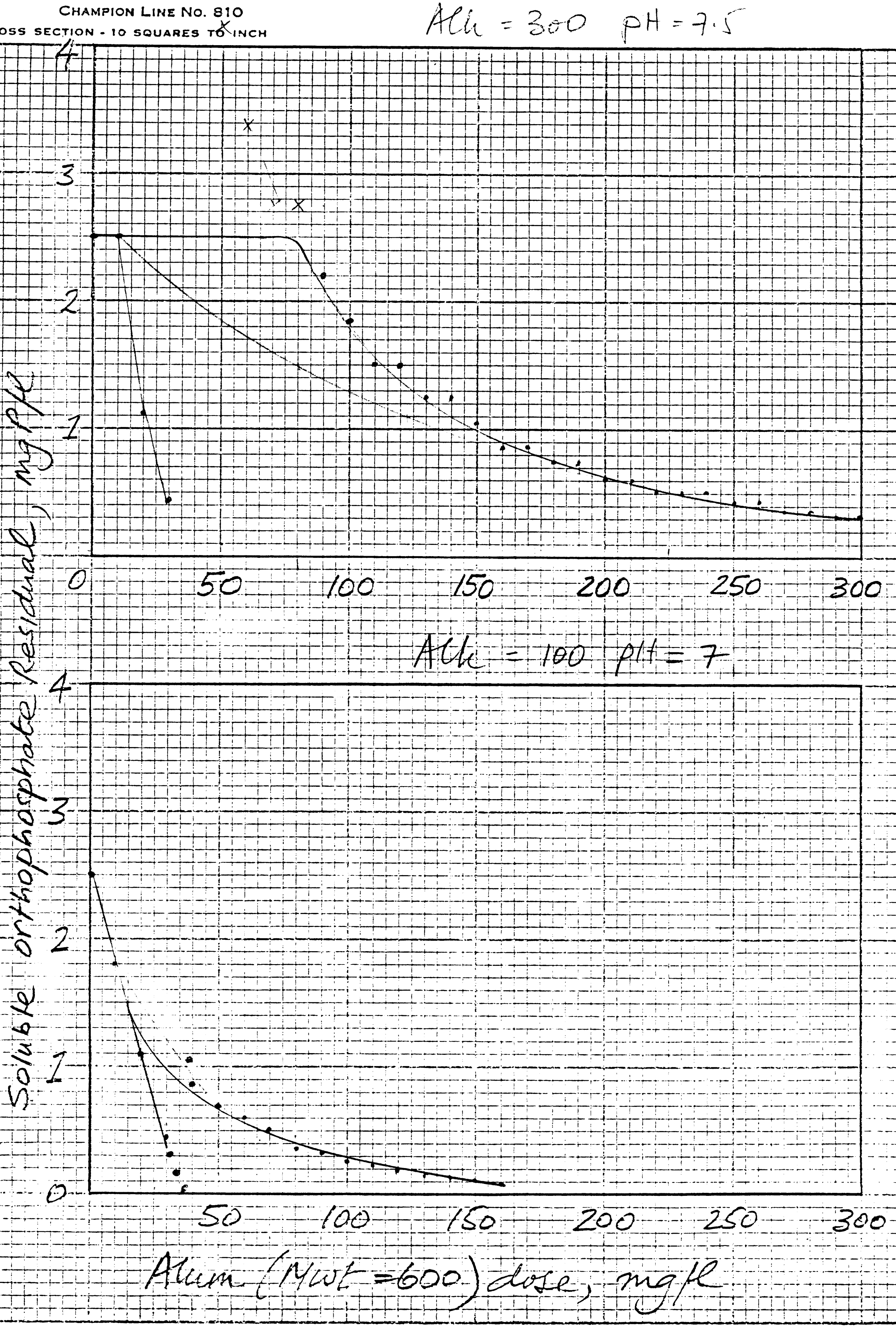


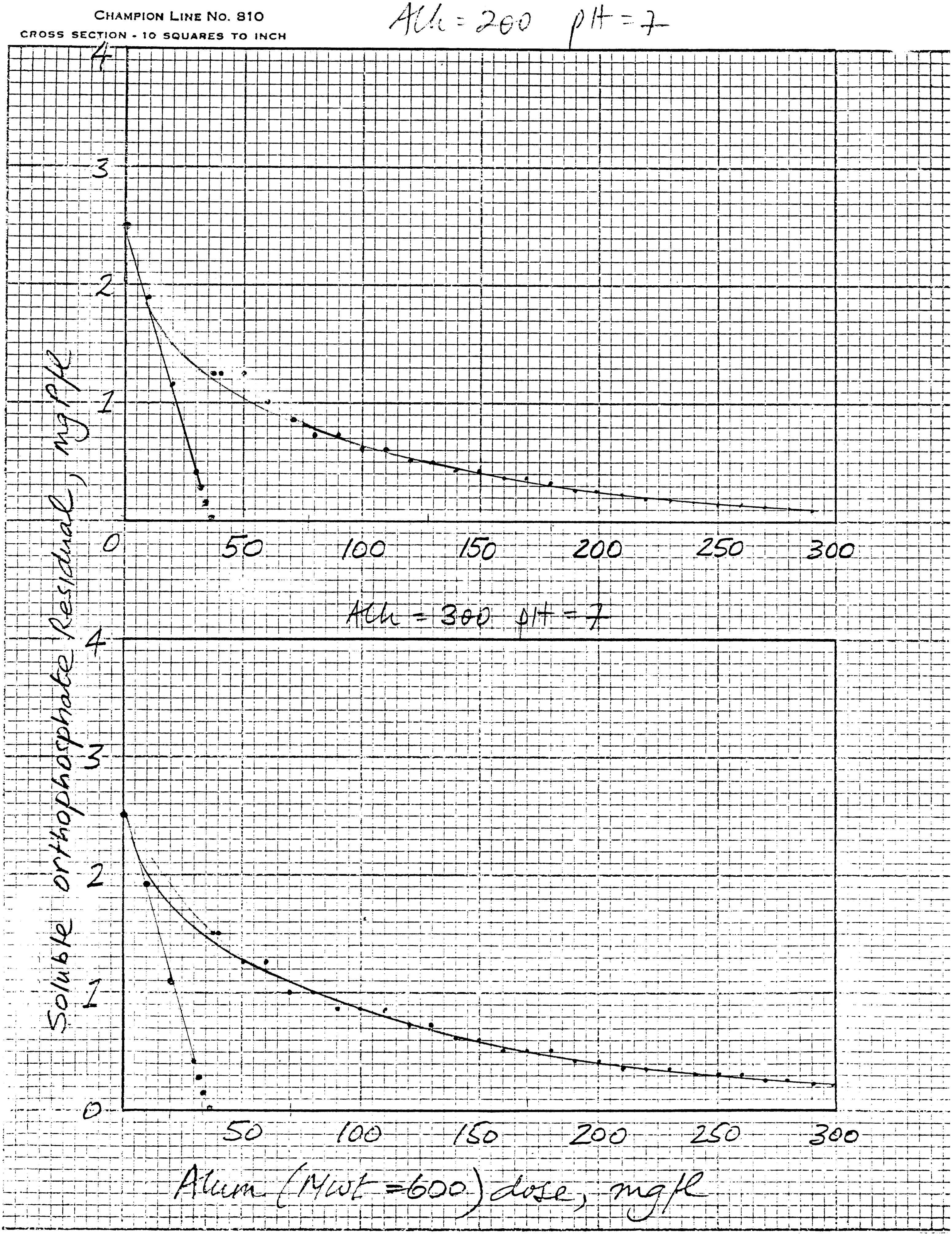
pH 7.5 Alk = 100

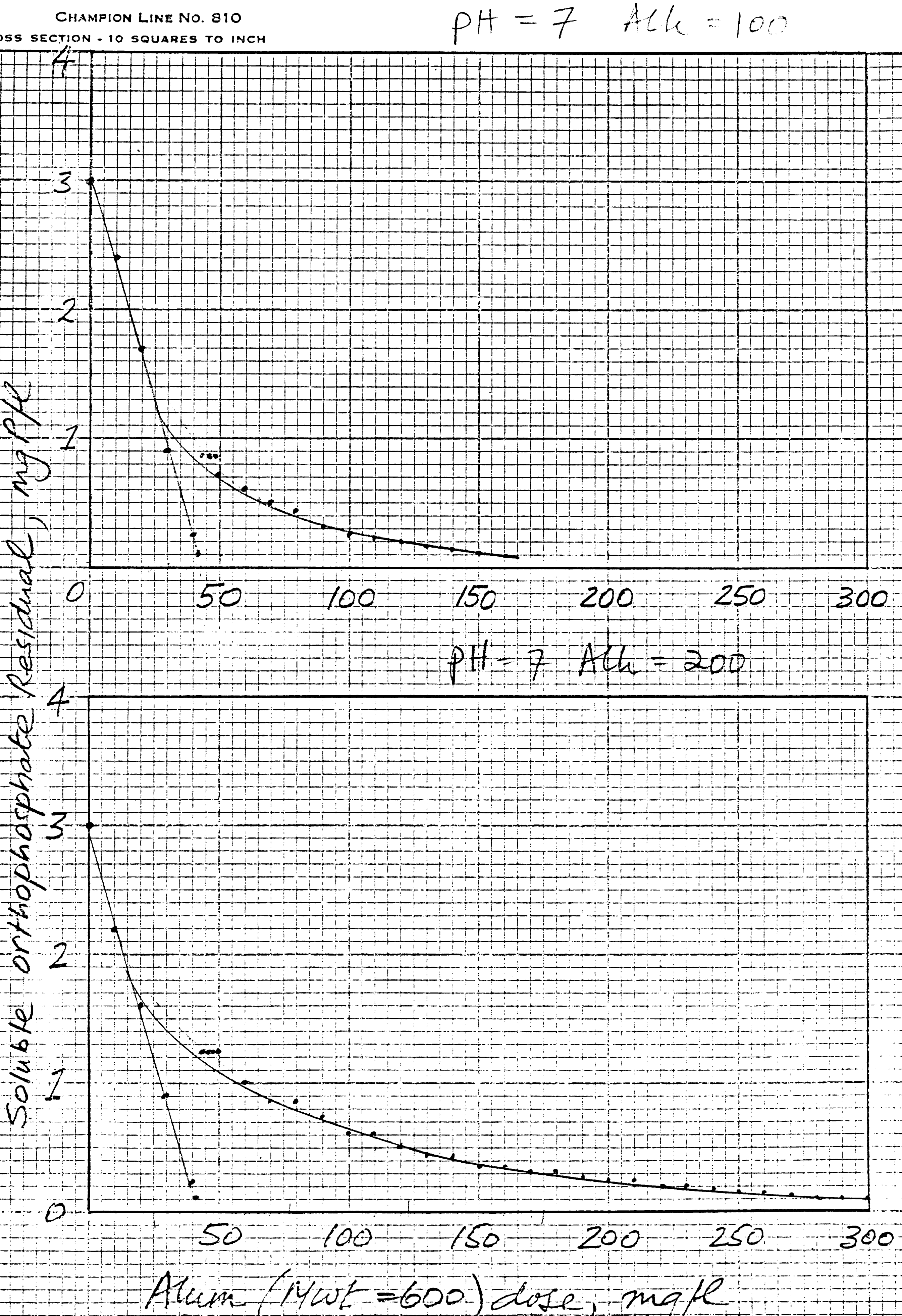


pH 7.5 Alk=200

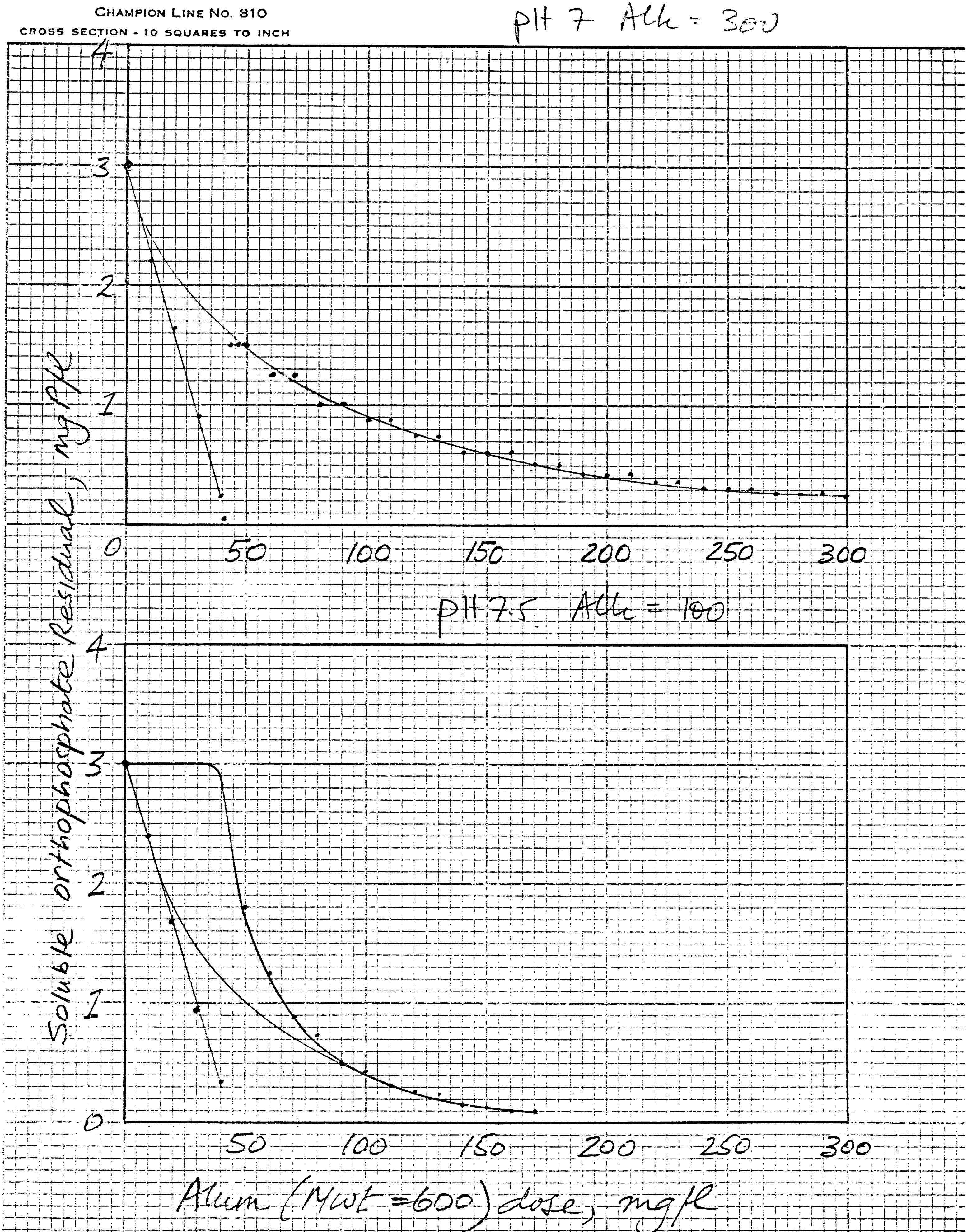



Alk = 300 pH = 7.5
4
3
2
1
0
50
100
150
200
250
300
Alk = 100 pH = 7
4
3
2
1
0
50
100
150
200
250
300
Soluble orthophosphate Residual, mg P/l
Alum (Mwt = 600) dose, mg/l

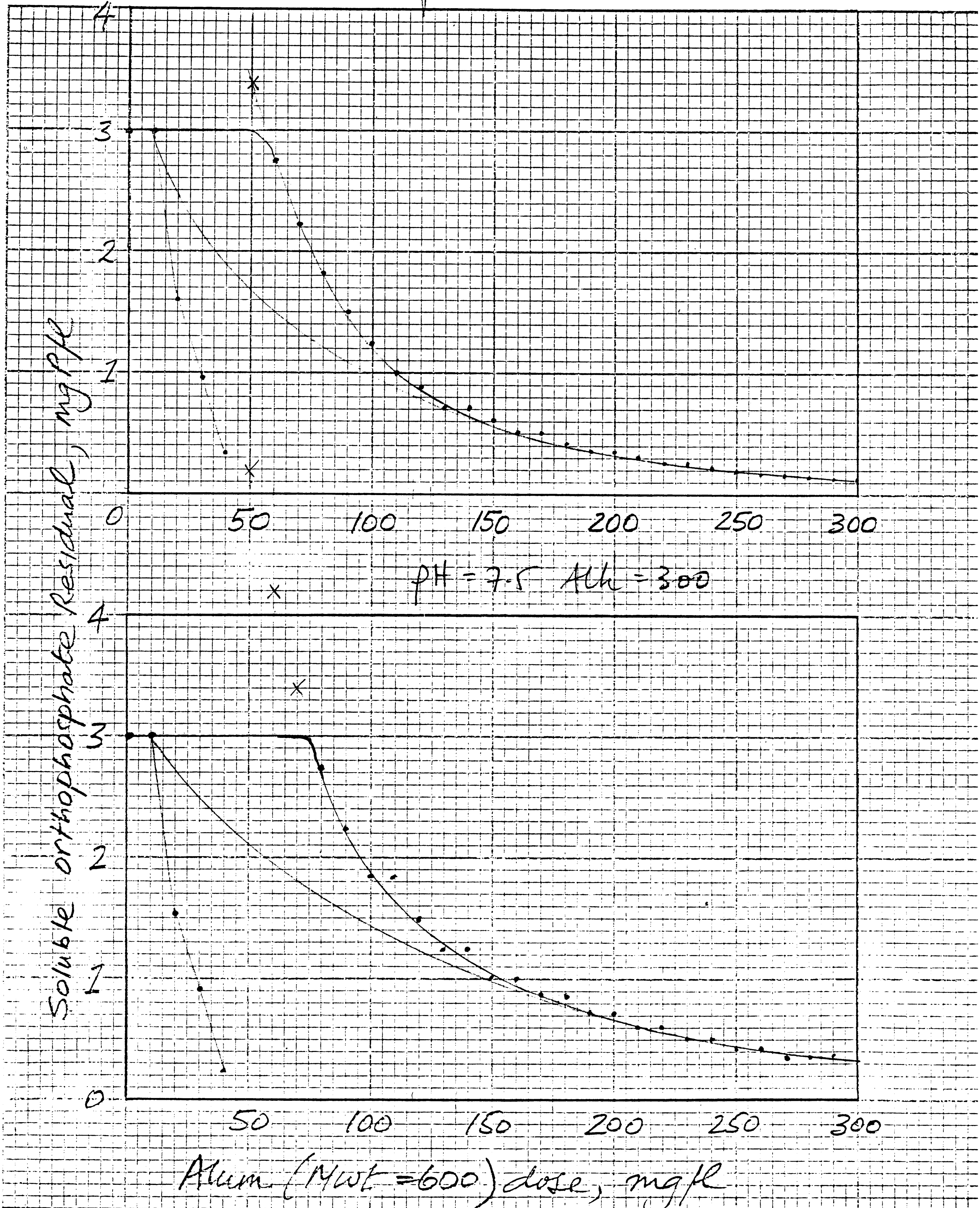

Alk = 200 pH = 7
Alk = 300 pH = 7
Soluble orthophosphate Residual, mg P/l
Alum (Mwt = 600) dose, mg/l
0
1
2
3
4
50
100
150
200
250
300


pH = 7 Alk = 100
pH = 7 Alk = 200
Soluble orthophosphate Residual, mg P/l
Alum (Mwt = 600) dose, mg/l
0
1
2
3
4
0
50
100
150
200
250
300

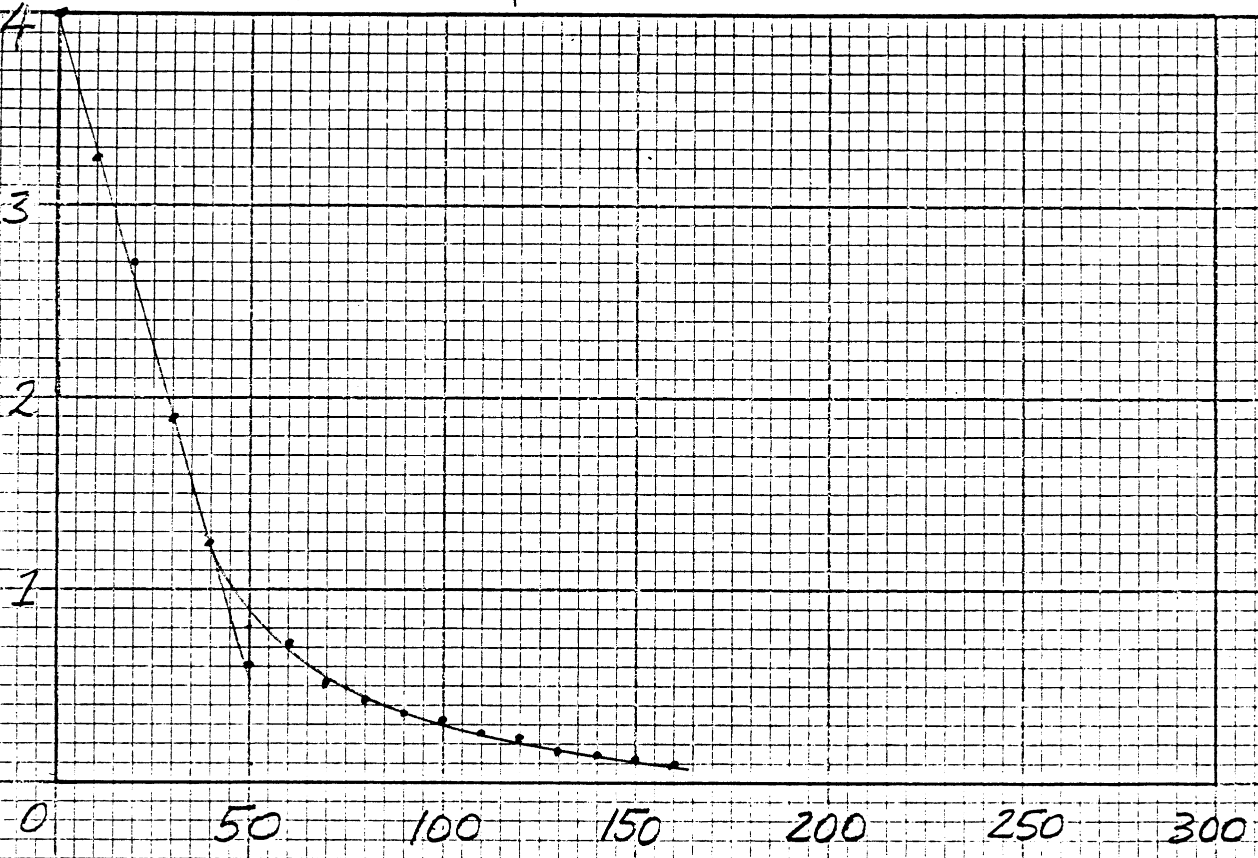
CHAMPION LINE NO. 810
CROSS SECTION - 10 SQUARES TO INCH



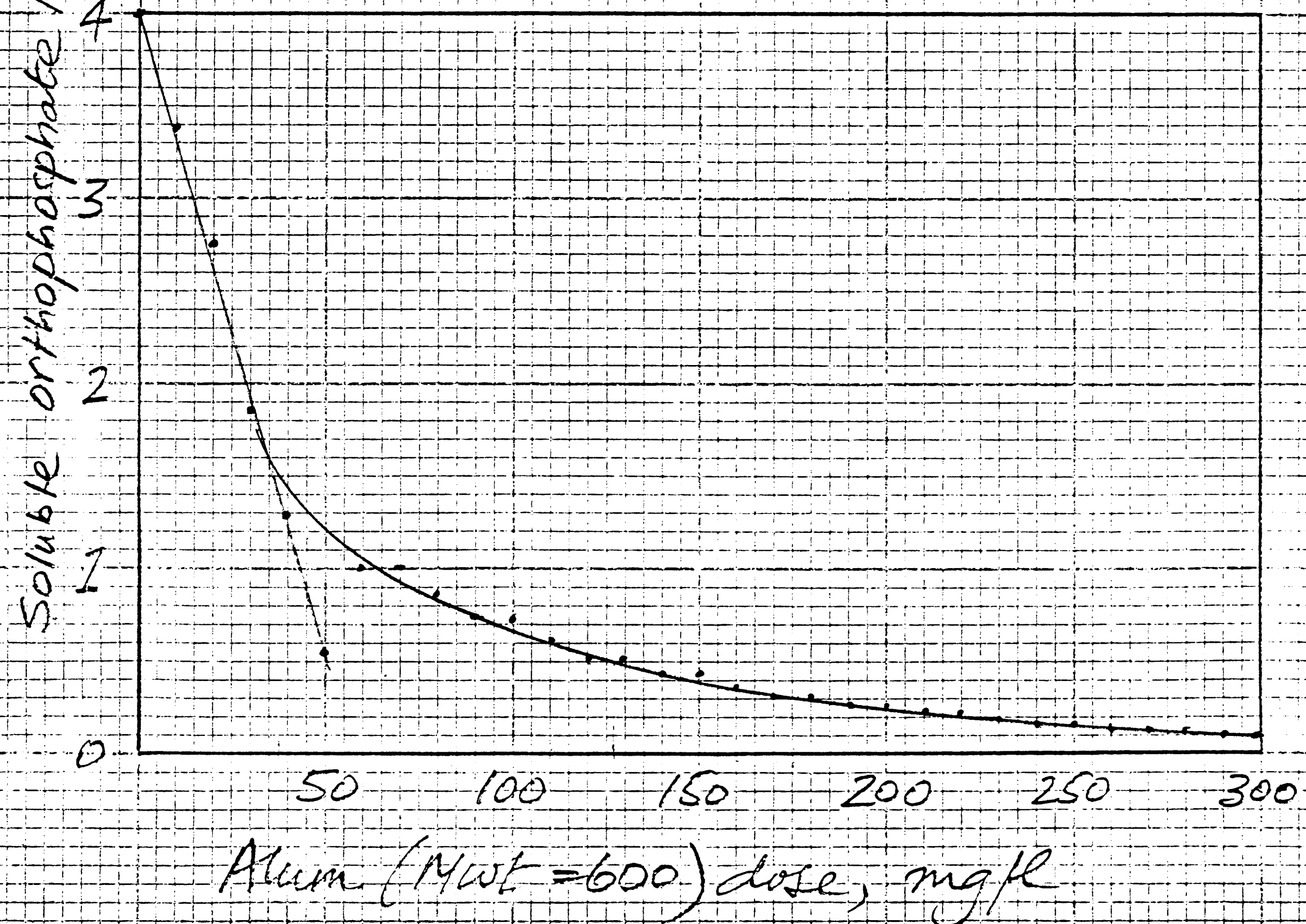
pH = 7.5 Alk = 200


4
3
2
1
0
50
100
150
200
250
300
pH = 7.5 Alk = 300
4
3
2
1
0
50
100
150
200
250
300
Soluble orthophosphate Residual, mg P/l
Alum (Mwt = 600) dose, mg/l

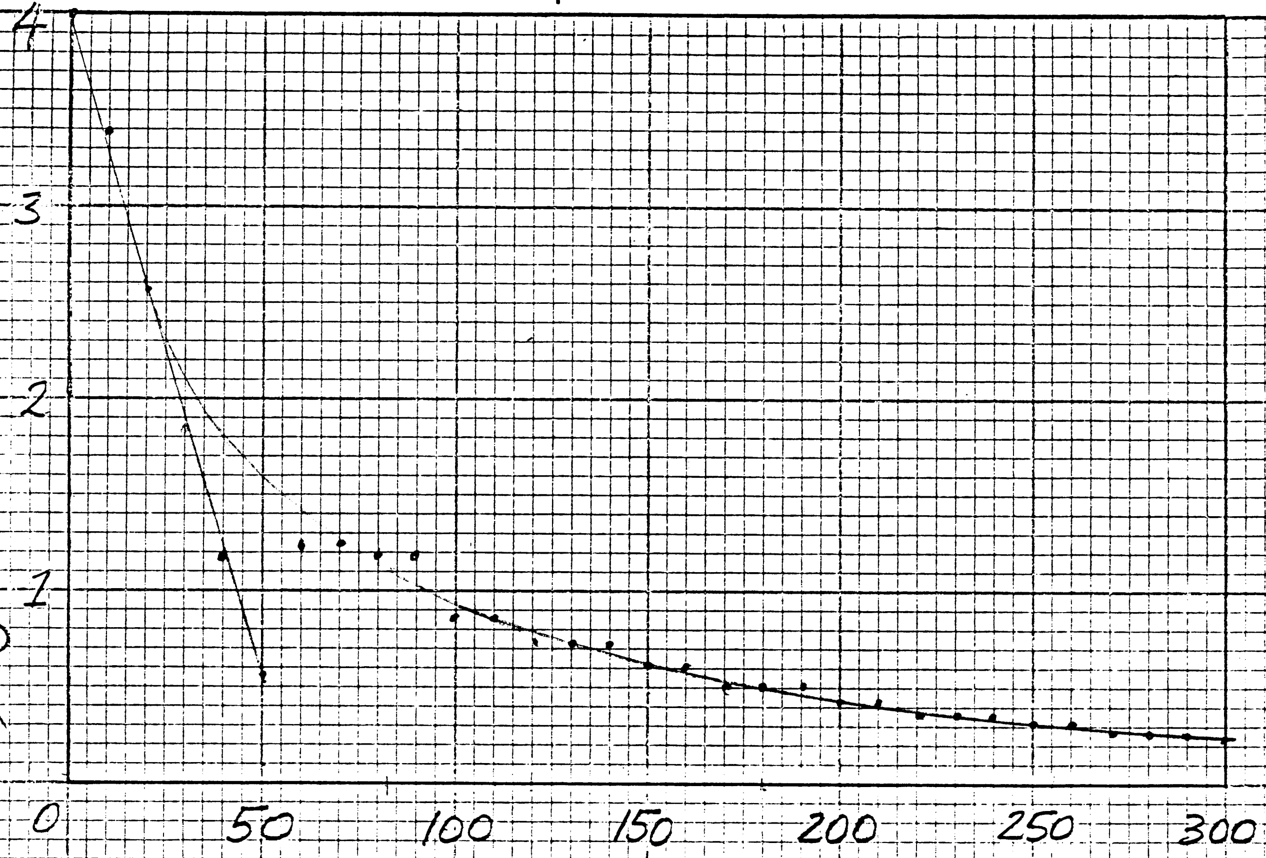
pH = 7 Alk = 100



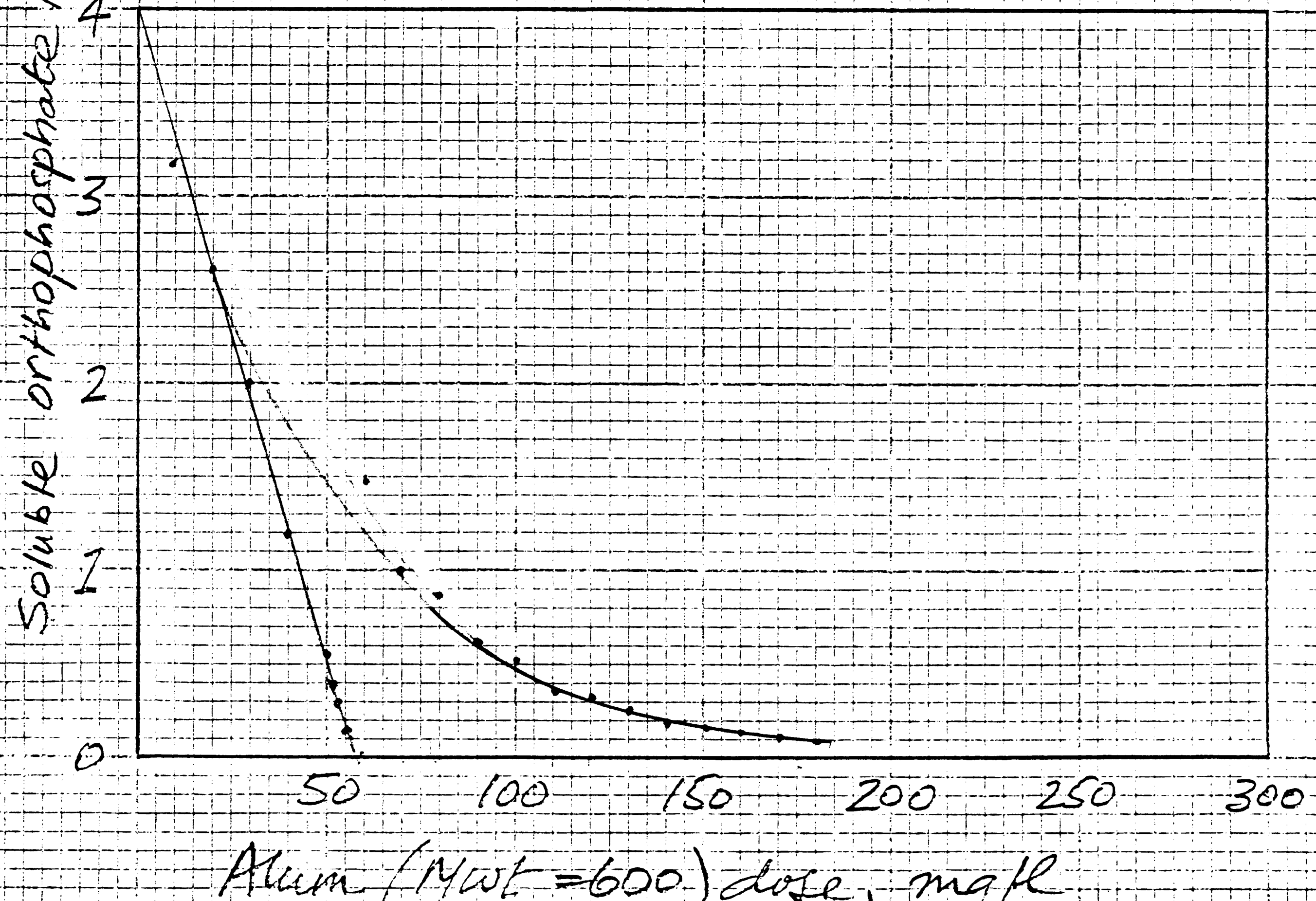
pH = 7 Alk = 200



pH = 7 Alk = 300



pH 7.5 Alk = 100



CHAMPION LINE No. 810

CROSS SECTION - 10 SQUARES TO INCH